4. Waste Characterization

4.1 INTRODUCTION

Proper characterization of the waste slated for disposal at the WIPP site is an essential element in assessing whether the repository meets the disposal standards set forth in 40 CFR part 191. To set the stage for the subsequent discussion, it is first necessary to define certain terms. Key definitions are as follows:

- A waste characteristic is a property of the waste that has an impact on the containment of the waste in the disposal system. Examples of waste characteristics include solubility of radionuclides, ability of the radionuclides to become part of stable colloids, gas generation potential from corrosion, microbial degradation or radiolysis, and various strength properties.

- A waste component is an ingredient of the total inventory of the waste that influences a waste characteristic. Examples of waste components include the quantity of metals, cellulosics and organic ligands, and the quantity of radioactivity (curies) associated with each radionuclide.

- Waste characterization is the process of determining the chemical, radiological, and physical properties of the waste. Waste characterization techniques include the use of process knowledge, laboratory and field experimentation, literature search, technical judgement, non-destructive examination/assay, and destructive analysis.

This chapter discusses the various regulations including 40 CFR part 191 which drive waste characterization, the ways in which waste characteristics can impact performance assessment (PA), the methods used for characterizing the waste, and the rationale for the waste characterization requirements of the 40 CFR part 194 rule.

4.1.1 Brief History of DOE's TRU Waste Characterization Program

DOE's TRU waste characterization program is based on the requirements developed for the proper handling and disposal of TRU wastes intended for the WIPP. Historically, this characterization has focused on two types of techniques; empirical — laboratory analyses to quantify hazardous and radioactive waste constituents such as metals, volatile organic compounds, Pu-239, etc.; and, informational based — the use of process/acceptable knowledge derived from site operations to classify wastes according to established categories.

This report describes the various facilities at TRU waste generator sites that are dedicated to characterizing TRU wastes via routine or modified chemical and radiochemical analyses.[1] Consistent with the 40 CFR part 194 rule, these aspects relate to *waste components*, as defined above. However, this definition of waste characterization excludes *waste characteristics*, which have historically been addressed under experimental programs, such as the Actinide Source Term Program (ASTP). The definition of *waste characterization* must be expanded accordingly to include these other aspects. As discussed in subsequent sections, the current DOE waste acceptance criteria and waste characterization guidance documents do not address the requirements of 40 CFR part 194 concerning *waste characteristics*.

4.1.1.1 DOE WIPP Waste Acceptance Criteria (WAC)

DOE developed and published tentative criteria for the acceptance of TRU waste produced under the defense related programs (DOE91) in 1980. These criteria were developed to ensure the safety of all operations at the WIPP. The waste acceptance criteria document was intended to provide: 1) criteria for use in project design; 2) technical justification for the WAC; and 3) quantitative guidelines to be used by waste generators for certifying TRU wastes. The criteria do not specifically stipulate whether further waste treatment or processing will be required, but DOE recognized that this decision would have to be made in the future. Revision 4 of the WAC, published in 1991, included additional criteria relevant to waste transportation and regulatory requirements for hazardous waste in order to provide a single, comprehensive document for all parties involved with the shipment and handling of WIPP waste. These criteria are summarized in Table 4-1. Revision 4 of the WAC also describes the relationship among the various DOE guidance documents that address characterization of TRU wastes, including the WIPP TRU Waste Characterization Quality Assurance Program Plan (TRU QAPP) (DOE94b) and the generator and/or storage site Quality Assurance Project Plans (QAPjPs). However, as discussed below, the WAC document is outdated and is not integrated with the TRU QAPP.

The Waste Acceptance Criteria Certification Committee (WACCC) is responsible for developing the WIPP WAC and verifying compliance of TRU waste with the WIPP WAC at the generator/storage facilities. According to DOE, compliance will be demonstrated

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[1] Many standard analytical protocols have been modified to accommodate the analytical and radiological aspects of analyzing materials heavily contaminated with Pu-239.

through audits and surveillances at waste generators (DOE91). It should be noted that WAC

Table 4-1. Summary of Waste Acceptance Criteria and Requirements[1]

WAC Criterion/ Requirement & Section	CH or RH	WIPP Operations and Safety Criteria	Transportation: Waste Package Requirements: TRAMPAC/RH-Cask[2]	RCRA Requirements	Performance Assessment Criteria
Waste Container Requirements/Criteria					
Waste Containers 3.2.1	CH	***Type A, Noncombustible***	***55-gal drums, SWBs, or SWB Overpack of 55-gal Drums or Test Bin***	No Additional Requirements	Same as Transportation
	RH	***Type A, Noncombustible***	***RH Canister***	No Additional Requirements	None
Waste Package Size 3.2.2	CH	Maximum dimension specified	***55-gal Drums in Two Seven Packs, of Two SWBs***	None	Same as Transportation
	RH	***RH Canister***	RH Canister	None	None
Waste Package Handling 3.2.3	CH	Drum and Box Handling Attachments	***Seven Packs, or SWBs***	None	No Additional Requirements
	RH	***Axial Pintle***	Axial Pintle	None	None
Waste Form Requirements/Criteria					
Immobilization 3.3.1	CH & RH	***≤ 1% Below 10 Microns, ≤ 15% Below 200 Microns***	None	No Additional Requirements	Same as WIPP Operation
Liquids 3.3.2	CH & RH	***Only Residual Liquids (see definitions in Section 3.3.2.1)***	< 1 Volume Percent	No Additional Requirements	< 1 Volume Percent
Pyrophoric Materials 3.3.3	CH & RH	≤ 1% Radionuclides, No Non-Radionuclide Pyrophorics	***≤ 1% Radionuclides, No Non-Radionuclide Pyrophorics***	***See Section 3.3.5.3***	Same as Transportation
Explosives and Compressed Gases 3.3.4	CH & RH	Not Permitted, 49 CFR 173 Subpart C and G	***Explosives and compressed gases are not permitted***	***See Section 3.3.5.3***	No Additional Requirements

Table 4-1. Summary of Waste Acceptance Criteria and Requirements (Continued)

WAC Criterion/ Requirement & Section	CH or RH	WIPP Operations and Safety Criteria	Transportation: Waste Package Requirements: TRAMPAC/RH-Cask[2]	RCRA Requirements	Performance Assessment Criteria
Waste Form Requirements/Criteria (Cont.)					
TRU Mixed Wastes 3.3.5	CH & RH	***Hazardous Waste must be Reported***	***Corrosives are not permitted***	***WIPP RCRA parts A & B Permit Applications, WAP, NMD***	No Additional Requirements
Specific Activity of Waste 3.3.6	CH	***> 100 nCi/g TRU***	Same as WIPP Operations	None	Same as WIPP Operations
	RH	***> 100nCi/g TRU ≤ 23 Ci/liter total***	Same as WIPP Operations	None	Same as WIPP Operations
Waste Package Requirements/Criteria					
Waste Package Weight 3.4.1	CH	< 21,000 lbs	***1000 lbs per drum, 4000 lbs per SWB, 7265 lbs per TRUPACT-II payload, 19,250 lbs per TRUPACT-II, 80,000 lbs GVW (DOT)***	None	None
	RH	***< 8,000 lbs***	RH-Cask TBD	None	None
Nuclear Criticality (Pu-239 FGE) 3.4.2	CH	See List in 3.4.2.1	***< 200 g/drum < 325 g/SWB, or < 325 g/TRUPACT-II***	None	Same as Transportation
	RH	≤ 600 g	***< 325 g/cask***	None	Same as Transportation
Pu-239 Equivalent Activity 3.4.3	CH & RH	***≤ 1000 PE-Ci/ package***	None	None	None
Surface Dose Rate 3.4.4	CH	***≤ 200 mrem/hr***	***≤ 200 mrem/hr, DOT Package Limits, and Shielded Packages per SARP***	None	Same as WIPP Operations
	RH	***95% ≤ 100 rem/hr. 5% ≤ 1000 rem/hr.***	RH-Cask TBD and DOT Package Limits	None	None

Table 4-1. Summary of Waste Acceptance Criteria and Requirements (Continued)

WAC Criterion/ Requirement & Section	CH or RH	WIPP Operations and Safety Criteria	Transportation: Waste Package Requirements: TRAMPAC/RH-Cask[2]	RCRA Requirements	Performance Assessment Criteria
Waste Package Requirements/Criteria (Cont.)					
Removable Surface Contamination 3.4.5	CH & RH	***≤ 50 pCi/100 cm² alpha, ≤ 450 pCi/100 cm² beta-gamma***	None	None	Same as WIPP
Thermal Power 3.4.6	CH	No Limit Report if > 0.1 watts/ft³	***Refer to Limits in TRUPACT-II SAR Section 1.2.3.3***	None	Same as Transportation
	RH	***≤ 300 watts/canister***	RH-Cask TBD	None	None
Gas Generation 3.4.7	CH	Vented	***TRAMPAC Limits: See requirements in Section 3.4.7.2, ≤ 500 ppm Flammable VOCs; Chemical compatibility study; all trace chemicals < 5 weight percent***	NMD Requirements Apply	SNL Test Plan
	RH	Vented	RH-Cask TBD	None	Same as CH
Labeling 3.4.8	CH	***Id Number, DOT***	***Id Number and Waste Shipping Category***	Same as DOT	None
	RH	***Id Number, DOT***	RH-Cask TBD	TBD	None
Data Package Requirements/Criteria					
Data Package/ Certification 3.5.1	CH	***Certification, WWIS Information, Data Format***	***Tables 13.1 to 13.3 in Appendix 1.3.7 (TRAMPAC)***	***Hazardous Waste Manifest per 40 CFR part 262 NMD and QAPP Requirements***	***PA Data Package, QAPP Requirements***
	RH	***Certification, WWIS Information, Data Format***	RH-Cask TBD	TBD	None

Table 4-1. Summary of Waste Acceptance Criteria and Requirements (Continued)

WAC Criterion/ Requirement & Section	CH or RH	WIPP Operations and Safety Criteria	Transportation: Waste Package Requirements: TRAMPAC/RH-Cask[2]	RCRA Requirements	Performance Assessment Criteria
Other Requirements/Criteria					
Additional Requirements 3.6.1	CH	None	***One Shipping Category per TRUPACT-II, Authorized TRUCON Content Codes, Waste Aspirated per SARP, Payload Control Procedures***	Regulations or Permit Conditions as Determined by NMED	None
	RH	None	RH-Cask TBD	TBD	None

1 - Limiting parameters are shown in bold italics.
2 - RH Cask limits have been finalized.

Source: Waste Acceptance Criteria for the Waste Isolation Pilot Plant (DOE91)

audits have not been performed at waste generator sites for the last two years. Historically, the WIPP WAC has been disconnected from waste characterization activities at the generator sites, precluding a prospective incorporation of WAC related requirements in generator site's ongoing waste generation practices. DOE plans to integrate the WAC in site waste generation activities in support of its greater reliance on process knowledge as the main waste characterization tool for newly generated wastes (DOE94d). The TRU waste generator sites differ in their individual approaches to the generation and characterization of TRU waste.

4.1.1.2 WIPP TRU QAPP

DOE released Revision B of the TRU QAPP in July, 1994. This document replaced the Waste Characterization Program Plan for WIPP Experimental Waste and the Quality Assurance Program Plan for the WIPP Experimental Waste Characterization Program. In the TRU QAPP, DOE

> identifies the quality of data necessary, and techniques designed to attain and ensure the required quality, to meet the specific objectives associated with the Department of Energy (DOE) Waste Isolation Pilot Plant (WIPP) Transuranic Waste Characterization Program (DOE94b).

This document provides guidance for the TRU waste generator sites in developing their site-specific QAPjPs. The QAPjPs contain detailed information regarding how the site will achieve the data quality objectives (DQOs) for the various waste characterization techniques. It is worth noting that neither this document nor the DOE Carlsbad Area Office's (CAO) guidance on the use of acceptable knowledge provides DQOs for waste characterization performed using acceptable knowledge (DOE94b, DOE95c).

4.2 REGULATORY DRIVERS FOR WASTE CHARACTERIZATION

This section briefly summarizes the various laws, regulations, and agreements which underlie the WIPP WAC and the specific waste characterization requirements which are distilled from these sources. The sources discussed include:

- Agreement for Consultation and Cooperation between DOE and the State of New Mexico
- The WIPP Land Withdrawal Act (LWA)
- NRC regulations for the packaging and transportation of radioactive waste (10 CFR part 71)
- Department of Transportation regulations
- Resource Conservation and Recovery Act and amendments
- The Federal Facilities Compliance Act (FFCA) of 1992
- EPA Toxic Substance Control Act regulations
- EPA 40 CFR part 191
- EPA WIPP compliance criteria (40 CFR part 194)

From the summary it will be clear that waste characterization, in various forms, is required not only to satisfy 40 CFR parts 191 and 194, but a variety of other regulations and agreements as well.

In certain instances, the regulatory framework separates the radioactive waste into two categories: 1) contact-handled transuranic waste (CH-TRU) and 2) remote-handled transuranic waste (RH-TRU). Definitions and restrictions applicable to each type of radioactive waste are presented in the ensuing discussion, where appropriate.

4.2.1 Agreement for Consultation and Cooperation—July 1, 1981

An Agreement for Consultation and Cooperation (the Agreement) between the State of New Mexico and the U.S. Department of Energy was signed by the parties on July 1, 1981. Appendix B to this Agreement is entitled Working Agreement for Consultation and Cooperation (the Working Agreement). Article IV of the Working Agreement provides a basis for the State to comment on waste acceptance criteria as described in IV.E.1.(c):

> DOE has provided this documentation to the State. Any State comments as to public health and safety concerns shall be provided to the DOE WIPP Project Manager within ___[2] calendar days after receipt of documentation from DOE. DOE shall respond to the State comments within ___[2] calendar days after receipt of such comments. Nothing herein shall preclude further discussions of the matter or any updates prepared by DOE. Reasonable time frames for State comments and DOE response to any DOE updates shall be negotiated by the principal representatives of the parties.

The Agreement and the Working Agreement were modified in November 1984 under the First Modification to the July 1, 1981 "Agreement for Consultation and Cooperation" on the WIPP by the State of New Mexico and the U.S. Department of Energy. Article VI.B of the Agreement was revised to set certain limitations on remote-handled transuranic waste including the following maximum values for specified parameters:

- volume — 250,000 cubic feet[3]
- surface dose rate — 1,000 rem/h
- volume with surface dose greater than 100 rem — 12,500 cubic feet
- activity level (averaged over canister volume) — 23 Curies (Ci)/l
- amount of radioactivity — 5.1 million Ci

The First Modification further specified that the concentrations of radionuclides in the RH-TRU canisters would be determined by one or more of the following methods: "(1) materials accountability; (2) classification by source; (3) gross radioactivity measurements; (4) direct measurements of major contributing radionuclides; or (5) such other methods as the parties may agree to."

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[2] To be negotiated in original agreement.

[3] This is 4% of the total waste volume.

A second modification to the Agreement was implemented on August 4, 1987 which included, among other things, amendment of Article VI.E to contain the following paragraph:

> "4. The transportation of radioactive waste to WIPP shall comply with the applicable regulations of the U.S. Department of Transportation and any applicable corresponding regulations of the U.S. Nuclear Regulatory Commission. All waste shipped to the WIPP will be shipped in packages which the Nuclear Regulatory Commission has certified for use."

4.2.2 WIPP LWA

The WIPP LWA was signed into law on October 30, 1992. Several items in the LWA relate to waste characterization including relevant definitions and limitations (particularly those involving RH-TRU waste). The following definitions from Section 2 of the LWA are important to waste characterization:

> "(20) TRANSURANIC WASTE — The term "transuranic waste" means waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes per gram of waste, with half lives greater than 20 years, except for—
>
> > (A) high-level radioactive waste
> >
> > (B) waste that the Secretary has determined with the concurrence of the Administrator, does not need the degree of isolation required by the disposal regulations; or
> >
> > (C) waste that the Nuclear Regulatory Commission has approved for disposal on a case-by-case basis in accordance with part 61 of title 10, Code of Federal Regulations."[4]
>
> "(3) CONTACT-HANDLED TRANSURANIC WASTE — The term "contact-handled transuranic waste" means transuranic waste with a surface dose rate not greater than 200 millirem per hour."

[4] The apparent intent of exceptions (B) and (C) is to preclude shipment to the WIPP of wastes which meet the transuranic waste definition, but can be properly disposed in other than a geologic repository (e.g., greater than Class C wastes (as defined in §61.55)).

> "(4) REMOTE-HANDLED TRANSURANIC WASTE — The term "remote-handled transuranic waste" means transuranic waste with a surface dose rate of 200 millirem per hour or greater."[5]

Section 7 of the LWA imposes the following waste-related limitations:

- Restrictions of remote-handled transuranic waste (RH-TRU)
  - 1,000 rem/h maximum surface dose rate
  - surface dose rate less than 100 rem/h for 95% by volume of all RH-TRU
  - Canister activity limited to 23 Ci/liter (averaged over the canister volume)
  - Total RH-TRU radioactivity is limited to 5.1×10^6 Ci

- Repository capacity — 6.2 million cubic feet of transuranic waste

Most of the waste requirements in Section 7 are also included in the First Modification to the Agreement for Consultation and Cooperation between DOE and the State of New Mexico (Section 4.2.1 above).

In Section 12, Congress made clear its intent that disposal at the WIPP be limited to TRU wastes by prohibiting the shipment and disposal of high-level radioactive waste or spent nuclear fuel.[6] In Section 16, it further specified that the TRU waste must be shipped to the WIPP in containers whose design is certified by NRC and whose QA requirements meet NRC standards.

[5] According to the LWA definitions of CH-TRU and RH-TRU, waste with a surface dose of exactly 200 millirem per hour meets both definitions.

[6] These terms are defined in Section 2 of the Nuclear Waste Policy Act of 1982 as follows:
12. "High-level radioactive waste": (A) The highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such waste that contains fission products in sufficient concentrations; and (B) other highly radioactive material that the Commission, consistent with existing law, determines by rule requires permanent isolation.
23. "Spent nuclear fuel" means fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated for reprocessing.

4.2.3 NRC Regulations for the Packaging and Transportation of Radioactive Waste (10 CFR part 71)

In 10 CFR part 71, the NRC sets "(1) requirements for packaging, preparation for shipment, and transportation of licensed material; and (2) procedures and standards for NRC approval of packaging and shipping procedures for fissile material and for a quantity of other licensed material in excess of a Type A quantity"[7] (§71.0). Under this rule, packages must be approved for each specific use. Subpart D of the rule defines the contents of the application for approval of a transportation package. (In the case of WIPP, the application approval package is the Safety Analysis Report (SAR) for the TRUPACT-II Shipping Package. Revision 0 was issued in February 1989. The latest revision is No. 14 which was issued in October, 1994.) The package description in the approval application must include the following information with regard to the contents of the shipping package (§71.33):

- Identification and maximum radioactivity of the radioactive constituents
- Identification and maximum quantities of fissile constituents
- Chemical and physical form
- Extent of reflection, the amount and identity of nonfissile materials used as neutron absorbers or moderators, and the atomic ratio of moderator to fissile constituents
- Maximum normal operating pressure
- Maximum weight
- Maximum amount of decay heat
- Identification and volumes of any coolants

The DOE shipping package application for the TRUPACT-II Shipping Package has been assigned Docket No. 71-9218 by the NRC who issued a Certificate of Compliance No. 9218

[7] A Type A quantity is an amount of radioactive material which does not exceed certain isotope-specific limits stipulated in Appendix A of 10 CFR Part 71.

(DOE93a) for use of this container to ship CH-TRU.[8] Revision 5 (June 9, 1994) of this certificate specifies the following limitations on the contents of the TRUPACT-II based on the items from §71.33 listed above:

> "Dewatered, solid or solidified transuranic wastes. Waste must be packaged in 55-gallon drums, standard waste boxes (SWB) or bins. Waste must be restricted to prohibit explosives, corrosives, nonradioactive pyrophorics, and pressurized containers. Within a drum, bin, or SWB radioactive pyrophorics must not exceed 1 percent by weight and free liquids must not exceed 1 percent by volume. Flammable organics are limited to 500 ppm in the headspace of any drum, bin, or SWB."
>
> "Contents not to exceed 7,265 pounds including shoring and secondary containers, with no more than 1,000 pounds per 55-gallon drum and 4,000 pounds per SWB."
>
> "Fissile material not to exceed 325 grams Pu-239 equivalent with no more than 200 grams Pu-239 equivalent per 55-gallon drum and 325 grams of Pu-239 equivalent per SWB."
>
> "Decay heat must not exceed values specified in Tables 6.1 through 6.3 of "TRUPACT-II Content Codes," (TRUCON), DOE/WIPP 89-004, Rev. 6."
>
> "Physical form, chemical properties, chemical compatibility, configuration of waste containers and contents, isotopic inventory, fissile content, decay heat, weight and center of gravity, radiation dose rate must be limited in accordance with Appendix 1.3.7 of the application, "TRUPACT-II Authorized Methods for Payload Control," (TRAMPAC)."
>
> "Each drum, bin, or SWB must be assigned to a shipping category in accordance with Table 5, "TRUPACT-II Content Codes," (TRUCON), DOE/WIPP 89-004, Rev. 6, or must be tested for gas generation and meet the acceptance criteria in accordance with Attachment 2.0 of Appendix 1.3.7 of the application."

As noted above, the Certificate of Compliance specifies that waste properties are determined and limited according to the specifications in TRAMPAC. TRAMPAC (Appendix 1.3.7 to the SAR) is the document which provides acceptable methods for the preparation and

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[8] As of the date of publication of this document, the most recent revision to the TRUPACT-II Shipping Package Application is Revision 14 submitted to NRC by Westinghouse (on behalf of DOE) on October 14, 1994. The current revision and revision date for other related documents are as follows:

- TRUPACT-II Content Codes (TRUCON) - Revision 8, October 1994
- TRUPACT-II Safety Analysis Report (SAR) - Revision 14, October 1994
- Certificate of Compliance No. 9218 - Revision 6, March 30, 1995

characterization of payloads for transport in TRUPACT-II. Parameters for which TRAMPAC specifically identifies restrictions are as follows:

- Physical and chemical form of the CH-TRU waste
- Chemicals to ensure chemical compatibility between all constituents in a given shipment
- Maximum pressure in a package during a sixty-day transport period
- Amount of potentially flammable gases that might be present or generated in the payload during a sixty-day transport period
- Layers of confinement (e.g., plastic bagging) in payload containers
- Fissile material content for individual payload containers and the total package
- Decay heat for individual payload containers and the total package
- Weight of the individual payload containers and the loaded TRUPACT-II
- Center of gravity for the payload assembly to be transported in TRUPACT-II
- Dose rate of individual payload containers, the total package, and three loaded packages on a truck trailer

The foregoing discussion is specific to CH-TRU waste. Currently there is no approved shipping container for RH-TRU waste. DOE plans call for RH-TRU to be shipped in the RH-72B, which is a scaled down version (5/8 scale) of the NuPac 125B container certified by NRC and used to ship waste from Three-Mile Island Unit 2 (DOE93a).

The TRAMPAC provides some detail on how various parameters are to be tested. For example, Section 9.4, <u>Methods of Determination and Control of Radionuclides</u>, specifies five allowable methods for the identification and quantification of radionuclides in TRU waste including:

- passive gamma
- radiochemical assay using alpha and gamma spectroscopy
- passive neutron coincidence counting
- passive-active neutron assay

- calorimetry

Attachment 3.0 to the TRAMPAC discusses each of the allowable methods including typical errors, sensitivities, calibration standards, assay procedures, and operator training. These topics are addressed further in the WIPP Transuranic Waste Quality Assurance Program Plan (DOE94b) and the site specific Quality Assurance Project Plans.

4.2.4 U.S. Department of Transportation Regulations: 49 CFR part 173 — Shippers — General Requirements For Shipments and Packaging

The Department of Transportation (DOT) has jurisdiction over hazardous materials shipments affecting intrastate and interstate commerce (DOE93a). This authority is derived from the Hazardous Materials Transportation Act of 1975 as amended by the Hazardous Materials Transportation Uniform Safety Act of 1990. Subpart I of 49 CFR part 173 sets out DOT regulations for the shipment of radioactive materials. Basically, the DOT regulations provide that any package which meets the applicable requirements of NRC regulation 10 CFR part 71 is authorized for shipment (49 CFR 173.416(b)). The DOT regulations add no additional waste characterization requirements beyond those already imposed by the NRC.

4.2.5 Resource Conservation and Recovery Act (RCRA)

The Resource Conservation and Recovery Act of 1976 (RCRA) and the Hazardous and Solid Waste Amendments of 1984 (HSWA) provide the statutory framework for the regulation of hazardous wastes at the WIPP. Under HSWA, certain "listed" and "characteristic hazardous" wastes are prohibited from land disposal unless the wastes meet specified treatment standards or it can be demonstrated to a reasonable degree of certainty that there will be no migration of hazardous constituents from the disposal unit for as long as the wastes remain hazardous. Migration of hazardous constituents outside the unit boundary must not exceed health-based limits (EPA92). The approach being taken by DOE at the WIPP is to seek a no migration variance rather than meet the technology-based treatment standards.

Requirements of a petition to seek a no migration variance are set forth in 40 CFR part 268—Land Disposal Restrictions. Specific requirements (§268.6) which relate to waste characterization are:

> §268.6(a)(2) A waste analysis to fully describe the chemical and physical characteristics of the subject waste [must be provided]
>
> §268.6(b)(1) All waste .... sampling, test, and analysis data must be accurate and reproducible to the extent that state-of-the art techniques allow
>
> §268.6(b)(2) All sampling, testing, and estimation techniques for physical and chemical properties of the waste .... must have been approved by the Administrator
>
> §268.6(b)(3) Simulation models must be calibrated for the specific waste .... conditions and verified for accuracy by comparison with actual measurements.

The No Migration Guidance Manual for Petitioners (EPA92) elaborates on the waste analysis dictated under §268.6(a)(2) noting that "proper management of wastes for as long as they remain hazardous requires that potential incompatibilities and waste transformation mechanisms be assessed." Some additional guidance provided in the Manual regarding details of waste descriptions is summarized below:

- Waste types and sources
  - applicable waste codes (EPA and industrial)
  - waste-generating processes
  - hazardous constituents and their properties
  - quantities of waste to be disposed
  - rate of disposal
  - handling and storage practices

- Waste characteristics
  - potential for leachate formation
  - waste solubilities
  - hazardous-constituent vapor pressures
  - other factors affecting waste mobility
  - analytical testing results for 40 CFR part 261 Appendix VIII hazardous constituents reasonably expected to be present in the waste

- Waste incompatibilities
  - potential chemical interactions
  - identification and characteristics of reaction products

- Waste transformation mechanisms
  - biodegradation
  - photodegradation

- hydrolysis
- oxidation/reduction
- volatilization

In 1990, EPA granted DOE a conditional no migration variance to permit DOE to implement an underground test program with a limited quantity of actual TRU waste at the WIPP (55 FR 47700). DOE subsequently canceled the test program so the no migration variance was never exercised. However, some of the conditions imposed by EPA in this conditional variance are instructive as presaging future EPA requirements when DOE seeks a final no migration variance to dispose of TRU wastes in the repository.[9] It is recognized that the conditional variance was based on short-term no migration considerations over a ten-year test phase with particular focus on air emissions. Thus, some of the conditions specified in granting the variance may not be indicative of requirements for permanent disposal.

In granting the conditional variance, EPA imposed the following requirements relating to waste analysis:

> To ensure that each waste container had no layer of confinement which contains flammable mixtures of gases or mixtures of gases which could become flammable when mixed with air, samples of gas from the head space in each container must be analyzed for hydrogen, methane, and volatile organic compounds. It must also be demonstrated that the headspace gas is representative of the gas within all layers of confinement in a container.
>
> To ensure that the wastes to be emplaced are compositionally similar to the wastes on which the no migration petition was based, representative samples of headspace gas must be analyzed and compared to compositions supplied with the petition. If the results are not comparable, the waste may not be shipped to WIPP (without treatment or modification)

A key finding in the conditional no migration determination was that "if adequate data are not collected, EPA will not be in a position to approve any no-migration petition for the operational or post-closure phase." EPA clearly stated that further characterization of the waste would be required before a final no migration petition could be considered by the Agency. EPA noted that, at a minimum, wastes should be analyzed for 32 organic compounds and six metals (Cd, Cr, Pb, Se, Hg, Ag). Testing should include headspace analysis of all waste types for the organics and analysis of sludges for both organics and metals.

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[9] DOE submitted a draft petition to EPA for a disposal phase no-migration variance in May, 1995.

4.2.5.1 RCRA part B Permit Application

Since New Mexico is authorized by EPA to permit facilities which treat, store and dispose of radioactive mixed waste, the RCRA part B Permit Application must be submitted to the New Mexico Environment Department (NMED). In February 1991, DOE submitted a RCRA part B Permit Application for the Test Phase and in May 1995 (Revision 5) for the disposal phase.[10]

The draft part B Permit Application contains a Waste Analysis Plan which was prepared in accordance with EPA guidance (EPA94). According to the Permit Application (Revision 5), the following waste is unacceptable for management at the WIPP facility:

- Ignitable, reactive and corrosive waste (Free liquids, explosives, compressed gases, oxidizers, and non-radioactive pyrophorics are prohibited.)
- Headspace gas volatile organic compounds (VOCs) in concentrations resulting in emissions not protective of human health and the environment
- Incompatible wastes (Waste must be compatible with container, cask, and TRUPACT II materials as well as other waste.)
- Compressed gases
- Free liquids (Residual liquids in well-drained containers must be less than 1% by volume.)
- Waste with 50 parts per million or more of polychlorinated biphenyls (PCBs)
- particulate waste not solidified, stabilized, or consolidated
- Wastes with EPA codes not listed in the RCRA part A permit application

The Waste Analysis Plan further specifies all waste containers (for both newly-generated and retrievably-stored wastes) undergo headspace gas analysis for total VOC concentrations. Based on results and trends DOE may propose in the future to reduce the sampling frequency. Homogeneous solids and soil/gravel wastes will be periodically sampled for VOCs, semi-

[10] New Mexico's RCRA regulations (HWMR-7) mirror the Federal RCRA regulations.

volatile organic compounds, and metals. Debris wastes will be characterized on the basis of acceptable knowledge rather than examination and/or assay. The physical form of all retrievably-stored wastes will be determined by radiography or visual examination.

4.2.6 Federal Facilities Compliance Act of 1992 (Public Law 102-386)

The FFCA is an amendment to the Solid Waste Disposal Act (SWDA) (42 U.S.C 6981) which, among other things, imposes certain restrictions on DOE regarding the storage of mixed wastes.[11] After October 6, 1995, DOE can continue to store mixed waste without violation of Section 3004(j) of the SWDA only if a plan has been submitted to EPA, or to a state agency authorized by EPA to regulate the hazardous components of the mixed waste, and has been approved by the appropriate agency. An order requiring compliance with the plan must also have been issued. According to Sec. 102 © of the FFCA, the requirement does not apply to facilities subject to existing agreement, permit, administrative, or judicial order. For example, a tri-partite compliance agreement among DOE, EPA Region X, and the State of Washington exists for the Hanford Site which takes precedence (DOE94a). While the FFCA does not, per se, require waste characterization, the compliance plans may.

The FFCA does, however, require that DOE generate an inventory of mixed wastes. Some of the specified elements of this inventory include:

- a description of each type of mixed waste including the name of the waste stream.
- the EPA hazardous waste code for each type of mixed waste that has been characterized at each DOE facility[12]
- an inventory of each type of waste that has not been characterized by sampling and analysis at each DOE facility
- the basis of DOE's determination of the applicable hazardous waste code for each type of mixed waste and a description of whether the determination is based on sampling and analysis or on process knowledge

The FFCA also requires that DOE develop and submit Site Treatment Plans for the development of treatment capacity and technologies for handling mixed waste. Required inventory reports and plans are described in Section 3021 of the FFCA. Mixed waste

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[11] Mixed wastes are wastes which contain a hazardous component regulated under the Resource Conservation and Recovery Act and a radioactive component regulated under the Atomic Energy Act.

[12] EPA Hazardous Waste Codes are found in 40 CFR parts 260 - 270.

inventory reports have been completed (DOE94c) and Draft Site Treatment Plans have been summarized in a recent DOE report (DOE94a). The National Summary Report (DOE94a) noted that about one-third of the existing mixed TRU waste can probably be shipped to the WIPP without further treatment, but the balance will require additional treatment to meet the expected waste acceptance criteria. Thus, at least implicitly, the FFCA requirements will result in increased understanding of the characteristics of the waste destined for the WIPP. Existing and proposed DOE facilities to treat mixed TRU waste are as follows:

- Existing Facilities
    - Idaho National Engineering Laboratory
    - Rocky Flats Environmental Technology Site
    - Argonne National Laboratory - East
    - West Valley Demonstration Project[13]
- New Facilities
    - Hanford Site
    - Argonne National Laboratory - West
    - Idaho National Engineering Laboratory
    - Nevada Test Site
    - Rocky Flats Environmental Technology Site
    - Oak Ridge Reservation
    - Savannah River Site[14]

Comments derived from information contained in the Site Treatment Plans for several of these mixed TRU treatment facilities are noted below.

Rocky Flats Environmental Technology Site (RFETS)

RFETS estimates the following distribution of mixed TRU wastes (RFP94):

- Meets WIPP WAC and TRAMPAC — 52.4%
- Test and possibly repackage for TRAMPAC — 30%

[13] TRU wastes at West Valley are not defense related and therefore are not slated for disposal at the WIPP.

[14] According to DOE94a, Vol II, the Savannah River Site has deferred treatment until more definitive information is available regarding the WIPP WAC.

- Immobilize for WIPP WAC — 5.4%
- Neutralize for WIPP WAC — 4.4%
- Oxidize for WIPP WAC — 1.2%
- Incomplete data — 6.6%

According to the draft site treatment plan, RFETS proposes to construct a facility which will include capabilities for repackaging, immobilization, neutralization, and oxidation. This facility is planned for operation in 2008.

As noted above, approximately 30% of the RFETS waste will require testing to determine whether the gas-generation requirements of TRAMPAC (see Section 4.2.3) will be met.

Nevada Test Site (NTS)

Mixed TRU waste at the Nevada Test Site (NTS) was shipped there from Lawrence Livermore Laboratory between 1974 and 1990 (NTS94). Since this waste is poorly characterized and may be in oversized packaging, NTS is proposing to construct a TRU Waste Certification Building, which, if funded, would be operational in FY 1999. Operations will include breaching, sampling, and repackaging waste, and certifying that the containers meet the WIPP waste acceptance criteria.

Idaho National Engineering Laboratory (INEL)

INEL has identified 52 waste streams, some portion of which will require treatment to meet the WIPP WAC (IDA94). Facilities proposed to handle these projected needs include the Remote Mixed Waste Treatment Facility (RMWTF), the Idaho Waste Processing Facility (IWPF), and several Generator Treatment Plan (GTP) sites to handle small waste volumes. The IWPF is designed to include the following treatment technologies: stabilization, amalgamation, sizing, and incineration. The RMWTF is designed to handle RH- and CH-TRU wastes containing reactive metals.

Argonne National Laboratory - East (ANL-E)

ANL-E has a few cubic meters of acidic waste water which must be treated in a proposed precipitation/filtration unit prior to shipment to WIPP (ANL94). The wastewater will be neutralized, heavy metals will be precipitated, and residual sludge will be stabilized. Other

ANL-E waste streams can be shipped without treatment.

Oak Ridge National Laboratory (ORNL)

ORNL is proposing the construction of a Waste Handling and Packaging Plant (WHPP) to handle five of its six waste streams (OAK94). The sixth waste stream is subject to CERCLA action under an existing agreement involving the State of Tennessee. The WHPP would contain a sludge mobilization facility which would fluidize waste from storage tanks and transfer it to the processing facility. In the processing facility, which consists mainly of a bank of hot cells, wastes will be remotely dried, assayed, packaged, and checked for contamination. Hot cell operation is dictated by the fact that a significant fraction of the ORNL wastes are RH-TRU. Start up tests for the WHPP are projected for 2005.

Other DOE Locations

Draft Site Treatment Plans at other TRU waste generator sites such as Lawrence Livermore and Los Alamos National Laboratories, the Savannah River Site, and the Mound Plant are much less specific as to planned actions.

4.2.7 TSCA: 40 CFR part 761— PCB Manufacturing, Processing, Distribution in Commerce and Use Prohibitions

Unlike the RCRA regulations, the TSCA regulations do not provide for the issuance of no migration variances. Thus, waste containing PCBs must be treated to meet TSCA requirements before disposal (IDA94). Generally speaking, §761.60—Disposal requirements—specifies that PCBs at concentrations of 50 ppm or greater must be treated in a licensed incinerator. Alternate methods of disposal which achieve the same level of performance in destroying PCBs as incinerators may be approved by EPA (§761.60(e)).

The draft site treatment plans prepared by INEL and Rocky Flats have noted that PCB-contaminated TRU waste at those facilities must be treated (IDA94 and RFP94). INEL states that wastes "will be treated to meet TSCA requirements" while Rocky Flats says that "PCBs must be destroyed or oxidized to meet WIPP WAC."

As discussed above in Section 4.2.5.1, Revision 5 of the WIPP RCRA part B Permit Application prohibits "waste with equal to or more than 50 parts per million (50 milligrams per liter) polychlorinated biphenyls (PCBs)." The Waste Analysis Plan indicates that transformer oils containing PCBs have been identified in a few waste streams included in the

organic sludges summary category and consequently these streams must be examined for PCBs.
Revision 1 of the WIPP Baseline Inventory Report (WTWBIR) states that 13 TSCA waste streams cannot be accepted at the WIPP under the terms of the draft RCRA part B Permit Application and are consequently excluded from the WTWBIR (DOE95a).

4.2.8 Environmental Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes (40 CFR part 191)

Subpart A, Environmental Standards for Management and Storage, of this rule sets annual dose equivalent exposure standards for the maximum off-site individual during facility operation as follows (50 FR 38085):

- whole body — 25 mrem
- thyroid — 75 mrem
- other critical organ — 25 mrem

These standards, coupled with DOE Order 6430.1-General Design Criteria, were used as the basis for setting the upper limit on TRU waste packages received at the WIPP at 1,000 Curies of Pu-239 equivalent activity[15] (DOE87). Inhalation dose calculations are based on particles having a 1 µm Activity Median Aerodynamic Diameter. Assumed accident scenarios set the particle size distribution for drum handling mishaps which, in turn, lead to a particle size specification in the WIPP WAC. Wastes not meeting the particle size specification mat require treatment prior to shipment to the WIPP. Distribution of drums of waste with high curie contents may be important in analyzing releases from drilling intrusions.

Subpart B, Environmental Standards for Disposal, and Subpart C, Environmental Standards for Ground-Water Protection, of the amended rule (58 FR 66414) prescribe the long-term containment requirements which the WIPP must meet and defines performance assessment as the basis for assessing compliance with the cumulative release limits in Subpart B. Performance assessment will establish, through iterative calculations, an envelope of waste acceptance criteria which, if met, should provide a reasonable expectation that the disposal

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[15] Pu-239 equivalent curies are used to normalize the inhalation hazard of various transuranic nuclides to that posed by Pu-239.

standards can be achieved for the regulatory life of the repository.

4.2.9 Criteria for the Certification and Re-certification of the Waste Isolation Pilot Plant's Compliance with the 40 CFR part 191 Disposal Regulations (40 CFR part 194)

The WIPP LWA orders EPA to promulgate, through a formal rulemaking process, the criteria which the Agency would use to assess DOE's compliance with the 40 CFR part 191 disposal standards at the WIPP. §194.24 of the rule deals with waste characterization and requires DOE to identify the chemical, radiological, and physical characteristics of all existing waste, and to the extent practicable, to-be-generated waste, proposed for disposal at the WIPP. DOE can use process knowledge, non-destructive examination/assay, and other methods to provide this waste description.

DOE is further required to substantiate that all waste characteristics which could impact containment of wastes by the disposal system have been identified and their impact assessed. Waste characteristics include, inter alia, radionuclide solubility, ability of radionuclides to exist in stable colloidal suspensions, gas generation potential, and shear strength. DOE must also substantiate that all waste components which influence the critical waste characteristics are identified and their impact assessed. Waste components include, but are not limited to, such items as the activity of each radionuclide, metals, cellulosics, cheating agents, and water and other liquids.

Using this information, DOE is required to set limits on those waste components judged to be important and to show that, when all of these components are set at the designated limits,[16] the disposal system will meet the numeric requirements of §191.34 and §194.55. It is then incumbent on DOE to ensure that the waste actually emplaced in the WIPP falls within these limits.

4.3 IMPACTS OF WASTE CHARACTERISTICS AND COMPONENTS ON PERFORMANCE ASSESSMENT

Generally speaking, waste characteristics are determined through laboratory and fields studies

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[16] In some cases, the upper limit on a component will produce the more conservative result while in other cases the lower limit will be controlling. For example, solubility of actinide elements generally increases as the pH of the solution is lowered. Thus one would want to specify the minimum quantity of components which would tend to increase pH.

or through literature assessment combined with technical judgement. Waste components tend to be measured on an on-going basis. As discussed in the following paragraphs, both waste characteristics and waste components can affect performance assessment.

4.3.1 Waste Characteristics

Waste characteristics can be broadly divided into four categories according to what they affect: mobility of actinide elements in solution, strength, fluid flow, and gas generation in the sealed repository (SAN92). These categories are discussed in general terms in this section and in more detail in sections 4.3.5 and 4.3.6.

4.3.1.1 Mobility in Solution

It is expected that under certain conditions the WIPP wastes will be exposed to brines. These brines can be the result of seepage of Salado Formation brines through the repository walls, seepage of brines from the overlying Rustler Formation through poorly sealed shafts or boreholes, or from flow of Castile Formation brines released by an inadvertent borehole (or boreholes) into the waste-filled rooms of the repository. The quantity of brine to which the waste is exposed is dependent on several factors including the stage of the creep closure of the room, the source of the brine, capillary effects, and the gas pressure in the room. The brine can mobilize the actinide elements in the waste by two mechanisms—solubility and formation of stable colloids. Solubility of the actinides is a complex function of brine strength, pH, oxidation state of the actinide species, carbon dioxide levels, and presence of organic ligands which can form soluble complexes with the actinides. Conditions for the formation of various types of stable colloids are still being examined in the laboratory. Once the actinide elements are mobilized, there are several conceptual mechanisms available by which they can be transported to the accessible environment. If the actinide elements are not mobilized in the brine, the only mechanism available for release from the disposal system is via waste-laden material brought to the surface as the result of inadvertent drilling.

4.3.1.2 Waste Strength

Waste strength enters into performance assessment calculations in several ways. The crushing resistance of the waste provides a back stress which opposes the creep closure of the bedded salt surrounding the waste and consequently slows the closure process. Room collapse, which is in part linked to crushing resistance, determines the porosity in the waste as a function of time. This porosity, in turn, is used in equations to calculate the flow of brine through the waste. In addition to the crushing resistance (i.e., volumetric plasticity as a function of pressure), other waste parameters needed for the constitutive equations used to calculate the waste response to stress are shear modulus, bulk modulus, and yield function constants. The constitutive parameters have been assumed based on educated guesses. While SNL believes these parameters are of secondary importance, they have recommended that bounding studies be conducted using extreme values of these parameters to provide an indication of disposal room response (LAB95). The crushing resistance has been obtained from laboratory experiments using simulated waste mixtures. From these experiments, a composite repository-wide curve of mean stress versus volumetric strain was developed based on an assumed waste weight mix of 28% metals (including the container), 28% combustibles, and 44% sludges (LAB95).[17] This curve was used in the 1992 WIPP Performance Assessment (PA) (SAN92, vol. 3, p. 2-71). Conceptually, the waste mix fits the definition of a waste component which influences a waste characteristic—the crushing resistance. Assessment of the response of the room to collapse also requires knowledge of the initial waste porosity. This waste characteristic can also be derived from the densities of the components which make up the waste.

The shear strength of the waste is needed to analyze the amount of waste which might be eroded from the wall of an intruding borehole by the action of the drilling fluid. Depending on the type of analysis performed, the tensile strength of the waste may also be needed to assess the amount of spallation which occurs in a borehole due to gas pressure release within the waste.

4.3.1.3 Gas Generation Within the Waste

Several mechanisms have been identified which can cause significant quantities of gas to be generated by the wastes after emplacement (BRU94). The principal gas generation mechanisms are related to the anoxic corrosion of certain metals and the anaerobic microbial degradation of cellulosics and other organic compounds. (Oxygen initially present when the disposal rooms are sealed is consumed in a reasonably short period producing an oxygen-free environment.) Quantities of gas produced by radiolysis and release of volatile organic

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[17] Based on information in DOE95a, the current weight fractions are 0.59 solid organics, 0.13 solid inorganics, and 0.28 sludges.

compounds are small by comparison.

The anoxic corrosion of ferrous metals requires the presence of water, which is consumed in the reaction while hydrogen is produced. This water can be initially present in the waste, brine which seeps into the disposal room from the surrounding formations, and/or brine which is released by an intruding borehole from a reservoir in the underlying Castile Formation. For gas generation to proceed at a significant rate, the ferrous metals must be inundated by water. The rate is reduced by three to four orders of magnitude when exposure is limited to water vapor. Aluminum and its alloys can be similarly involved in anoxic corrosion also producing hydrogen.

Microbial degradation of cellulosics and, perhaps, plastics and rubber, can produce a variety of gases including hydrogen, methane, hydrogen sulfide, carbon dioxide, and nitrous oxide. For this to happen, the following conditions must all be met:

- the microorganisms are present when the repository is sealed
- the microorganisms persist for a significant fraction of the 10,000-year repository life
- adequate water is present
- sufficient oxidants are present
- sufficient nutrients such as P and N are available

If the gas pressure generated by these mechanisms exceeds the lithostatic pressure of the surrounding rock formation (i.e., about 14.8 MPa or 150 atmospheres), several disposal system responses are possible. The relatively brittle anhydrite interbeds above and below the repository horizon could fracture providing enhanced pathways for transport of radionuclides to the accessible environment, the creep closure process could be reversed, and/or brine could be driven from the disposal rooms causing the gas-producing reactions to cease.

Recent work has shown that gas spallation processes can cause significant quantities of waste to be transported to the surface from an intruding borehole. These processes become significant when the pressure in the waste exceeds the fluid pressure of the drilling mud at the base of the borehole (about 8MPa).

4.3.1.4 Fluid Flow

SNL uses the computer code BRAGFLO to model two-phase flow in various regions of the repository. The mass balance equations in BRAGFLO employ effective permeability k_i which is the product of the intrinsic permeability and the relative permeability of the *i*th phase (i.e., gas or water). In the 1991 and 1992 WIPP performance assessments, the intrinsic permeability of the waste was set at $1x10^{-13}$ m^2 based on some experimental work with simulated waste (SAN92). The relative permeabilities of the gas and the liquid were derived from empirical composite curves based on measurements in many porous materials such as sand, sandstone, and clay as a function of liquid saturation (i.e., the amount of pore space in the waste occupied by liquid at any point in time). These empirical curves require assumptions as to the residual brine saturation, the residual gas saturation and a pore shape distribution parameter. In addition, the BRAGFLO equations also require specification of the capillary pressure which is assumed, based on an empirical relationship, to be a function of intrinsic permeability and a factor which reflects parametric uncertainty. Since no WIPP waste-specific data exist for capillary pressure or relative permeability, a high degree of parametric uncertainty exists for waste-related flow properties.

4.3.2 <u>Waste Components</u>

Waste components can be generally divided into those which influence certain waste characteristics thus indirectly influencing PA, and those which directly influence performance assessment. The former category would include such items as quantities of gas generating materials, physical waste composition (i.e., waste volume mix), and quantities of constituents affecting waste mobility (e.g, organic ligands). The total quantity of various actinide elements present in the waste will govern whether the amount of the actinide species mobilized in the waste is limited by the solubility of the element in intruding brines or by the total inventory of the element in the waste. Waste components which directly influence performance assessment generally relate to the quantities of radioactivity in the waste (i.e., its curie content).

The curie content of waste enters explicitly into performance assessment calculations in two ways. First, it is used to set the release limits in accordance with Table 1 of 40 CFR part 191. For TRU radionuclides, the release limits in Table 1 are based on one million curies of alpha-emitting transuranic radionuclides with half-lives greater than 20 years. Thus, if the WIPP repository hypothetically contained 5 million curies of TRU radionuclides, the release limits used in determining compliance with §191.13 would be five times the values listed in Table 1. A feature of 40 CFR part 191 is that the allowable release is linearly proportional to the amount of TRU waste emplaced in the repository. Second, the variability in the curie content from drum to drum may be used to calculate the variability in the quantity of radioactivity released to the land surface from a borehole which inadvertently intercepts the waste. The quantity of radioactivity in the waste also enters into performance assessment indirectly. For example, when coupled with the amount of brine in-flow into a disposal room, the quantity of radioactivity determines whether the concentration of a nuclide in solution is limited by solubility (including colloidal formation) or by the total radionuclide inventory.

At a more fundamental level, the quantity of radioactivity determines whether the waste meets that TRU waste definitional specification of 100 nanocuries per gram of waste. Wastes containing less than 100 nanocuries per gram are classified as low-level wastes and are excluded from disposal at the WIPP.

4.3.3 Current and Projected Waste Inventory at the WIPP

Waste destined for disposal at the WIPP is to be packaged in 55 gallon steel drums, Standard Waste Boxes (which are 1.9 m^3 steel containers designed to fit into a TRUPACT-II shipping package), and cylindrical canisters for RH-TRU. Based on a waste volume of 0.208 m^3 for a 55-gallon drum, the capacity of the repository is 846,000 drum equivalents.[18] Each disposal room within the repository is nominally slated to receive 6,804 drums.

According to Revision 1 of the WIPP Transuranic Waste Baseline Inventory Report (WTWBIR), the DOE TRU waste generator sites currently have in inventory 73,000 m^3 of CH-TRU and 1,200 m^3 of RH-TRU waste (DOE95a). Thus, the current inventory is approximately 41% of CH-TRU capacity and 17% of RH-TRU capacity. The sites expect to generate an additional 51,000 m^3 of CH-TRU waste and 3,600 m^3 of RH-TRU waste in the future. Since the current inventory plus the volumes of waste projected to be generated before repository closure are less than the statutory/regulatory capacity of the repository, DOE, for scoping purposes, scales the projected inventory so that the statutory capacity is

[18] The term drum equivalents is used to reflect the fact that not all the waste is packaged in 55-gallon drums. The drum-equivalent calculation assumes a repository volume of 176,000 m^3.

reflected in total inventory numbers. For example, since the currently anticipated RH-TRU volumes are 4,800 m^3, and the capacity as limited by DOE's agreement with the State of New Mexico is 7,080 m^3, an additional 2,280 m^3 of waste are added to the anticipated RH-TRU quantity to reach the repository limit.[19] CH-TRU is treated similarly. Details are presented in Table 4-2.

Table 4-2. Transuranic Waste Disposal Inventory for WIPP (Cubic Meters)

Waste Matrix Code Groups	Stored Volumes	Projected Volumes	Anticipated Volumes	WIPP Disposal Volumes
Contact Handled Waste				
Combustible	7.1E+03	2.7E+04	3.4E+04	6.2E+04
Filter	4.3E+02	1.1E+03	1.5E+03	2.6E+03
Graphite	6.7E+02	4.3E+01	7.1E+02	7.6E+02
Heterogenous	3.0E+04	4.6E+03	3.5E+04	3.9E+04
Inorganic Non-metal	1.2E+03	3.2E+02	1.5E+03	1.8E+03
Lead/Cadmium Metal Waste	5.6E+01	1.3E+02	1.8E+02	3.1E+02
Salt Waste	3.3E+01	6.0E+01	9.2E+01	1.5E+02
Soils	3.7E+02	4.5E+02	8.3E+02	1.3E+03
Solidified Inorganics	1.7E+04	8.0E+03	2.5E+04	3.4E+04
Solidified Organics	1.5E+03	3.0E+02	1.8E+03	2.1E+03
Uncategorized Metal	1.2E+04	8.6E+03	2.1E+04	3.0E+04
Unknown	1.7E+03	0.0E+00	1.7E+03	1.7E+03
Total CH Volumes	**7.3E+04**	**5.1E+04**	**1.2E+05**	**1.8E+05**
Remote Handled Waste				
Combustible	1.5E+01	3.2E+00	1.8E+01	2.0E+01
Filter	8.9E-01	2.1E+00	3.0E+00	4.3E+00
Heterogenous	4.4E+02	3.3E+03	3.8E+03	5.9E+03
Lead/Cadmium Metal Waste	0.0E+00	6.0E+00	6.0E+00	9.8E+00
Salt Waste	0.0E+00	2.8E+00	2.8E+00	4.6E+00
Solidified Inorganics	6.1E+02	1.7E+02	7.9E+02	9.0E+02
Uncategorized Metal	8.8E+01	8.6E+01	1.7E+02	2.3E+02
Unknown	1.1E+01	2.4E+01	3.5E+01	3.5E+01
Total RH Volumes	**1.2E+03**	**3.6E+03**	**4.8E+03**	**7.1E+03**
Total TRU Waste Volumes	**7.4E+04**	**5.4E+04**	**1.3E+05**	**1.8E+05**

Source: WTWBIR, Revision 1, Table 3-5

[19] In its WTWBIR documentation, Hanford submitted two "suspect" RH-TRU waste streams with a volume of 41,232 m^3. Since no radionuclide information was available on these streams, they were not included in the scale-up in Revision 1 of the WTWBIR, but it should be noted that the volume of these two streams is six times the allowable RH-TRU capacity of the repository.

TRU waste is a complex mixture of sludges, metals, combustibles such as paper and rags, soils, filters, graphite, etc. As discussed above, these waste components can influence actinide solubility, gas generation, and waste strength characteristics. Table 4-3 provides a comparison of the relative compositions of the CH-TRU and RH-TRU wastes based on the data in Table 4-2 (DOE95b).

Table 4-3. Estimated Composition[1] of Waste Disposal Inventory at WIPP Repository Capacity (DOE95b)

Final Waste Form	% Total CH Inventory	% Total RH Inventory	% Total CH-TRU and RH-TRU Inventory
Combustible	34	<1	33
Filter	1.4	<1	2
Graphite	<1	0	1
Heterogeneous Waste	22	83	24
Inorganic Non-Metal Waste	1	0	1
Lead/Cadmium Metal Waste	<1	<1	<1
Salt Waste	<1	<1	<1
Soil	1	0	1
Solidified Inorganics	19	13	19
Solidified Organics	1	0	1
Uncategorized Metals[2]	17	3	16
Unknown[3]	1	1	1

[1] Totals may not add to 100% due to rounding.
[2] Includes all metals/alloys except lead and cadmium.
[3] Waste is presently uncharacterized but will be characterized prior to shipment to WIPP.

In developing the information contained in Tables 4-2 and 4-3, DOE prepared profiles for approximately 360 waste streams at various generating sites. The profiles were then assigned to one of approximately 130 waste matrix codes (WMC) and the WMCs were categorized into one of thirteen Waste Matrix Code Groups (WMCG) (DOE95a). The WMC numbers and the WMCG descriptions are shown in Table 4-4.

Table 4-4. Waste Matrix Code Group Names
(Source: WTWBIR, Revision 1, Table 1-2)

Waste Matrix Code Group	Waste Matrix Codes
Solidified Inorganics	1000[1], 1100[1], 1110[1], 1120[1], 1130[1], 1140[1], 1190[1], 1200[1], 1210[1], 1220[1], 1230[1], 1240[1], 1290[1], 3000[2], 3100, 3110[3], 3111[3], 3112[3], 3113, 3115[3], 3116[3], 3119[3], 3120, 3121, 3122, 3123, 3124, 3125, 3129, 3130, 3131[3], 3132[1], 3139[1 or 3], 3150, 3190, 3900[2], 6100[4], 6120[5], 6130[6], 6140[5], 6190[4], 6200[7], 6210[8], 6230[8], 6290[7], 7300[3], 9100[2], 9200[2]
Salt Waste	3000[2], 3140, 3141, 3142, 3143, 3149, 3900[2]
Solidified Organics	2000[1], 2100[1], 2110[1], 2120[1], 2190[1], 2200[1], 2210[1], 2220[1], 2290[1], 2900[1], 3000[2], 3114, 3200, 3210, 3211, 3212, 3213, 3219, 3220, 3221, 3222, 3223, 3229, 3230, 3290, 3900[2], 6100[4], 6110[5], 6190[4], 6200[7], 6290[7], 9100[2], 9200[2]
Soils	4000, 4100, 4200, 4900
Uncategorized Metal (Metal Waste Other Than Lead and/or Cadmium	5000[9], 5100, 5110, 5190, 6200[7], 6220[8], 7000[10], 7490[11], 9300[10]
Lead/Cadmium Metal	5000[9], 5120, 5130, 6200[7], 6220[8], 7000[10], 7200, 7210, 7220, 7400[11], 7410[11], 7420[11], 9300[10]
Inorganic Non-Metal Waste	5000[9], 5200, 5210, 5220, 5230, 5240, 5290
Combustible	5000[9], 5300, 5310, 5311, 5312, 5313, 5319, 5320, 5330, 5390
Graphite	5000[9], 5340
Heterogenous	5000[9], 5400, 5420, 5430, 5440, 5450, 5490, 6200[7], 6220[8], 6290[7]
Filter	5000[9], 5410
Excluded Waste[12]	5250, 5350, 6300, 6400, 7100
Unknown[13]	8000, 8100, 8200, 8900

[1] Liquid waste streams are assumed to be solidified prior to sending to WIPP.
[2] WMCs 3000, 3900, 9100, and 9200 are placed in "solidified inorganics," "salt waste," or "solidified organics," depending on the information provided by the TRU waste generator/storage site.
[3] particulate waste streams are assumed to be solidified prior to sending to WIPP.
[4] WMCs 6100 and 6190 are placed in "solidified organics," or "solidified inorganics," depending on the information provided by the TRU waste generator/storage site.
[5] Liquid lab pack waste is assumed to be solidified prior to sending to WIPP.
[6] Solid lab packs are assumed to be solidified prior to sending to WIPP.
[7] WMCs 6200 and 6290 are placed in "solidified organics," "solidified inorganics," or "heterogeneous" if the waste stream must be solidified per the generator/storage site. They are placed in "uncategorized metal," or "lead/cadmium metal waste" if they are primarily nonreactive metal contaminated with reactive metal. Reactive waste streams must be treated prior to shipment to WIPP.
[8] Waste stream is assumed to be treated prior to sending to WIPP. Volume change is provided by the TRU waste generator/storage site.

[9] WMC 5000 is placed in "uncategorized metal," "lead/cadmium metal," "inorganic non-metal," "combustible," "graphite," "heterogeneous," or "filter," depending on the information provided by the generator/storage site.
[10] WMC 7000 and 9300 are placed in "uncategorized metal" or "lead/cadmium metal," depending on the information provided by the generator/storage site.
[11] WMCs 7400, 7410, 7420, and 7490 are assumed to be drained of liquid and contain only metal waste.
[12] These waste streams are excluded from disposal in WIPP at this time, e.g., PCB and asbestos wastes (see Table 3-2).
[13] If adequate information is provided by the generator/storage site, these WMCs are changed. If there is not enough information, these waste streams remain as "unknown" and are excluded from disposal in WIPP until characterized.

Because various waste material parameters (i.e., waste components) are important to performance assessment calculations, the WTWBIR provides estimates of the mix of materials expected in the inventory. For example, iron and aluminum are important to assess the amount of hydrogen gas which might be generated by anoxic corrosion if these metals are exposed to brine. The estimated ranges for these material parameters, expressed as material densities, are summarized in Table 4-5 for CH-TRU waste (DOE95a).

Table 4-5. WIPP CH-TRU Waste Material Parameter Disposal Inventory
(Table 5-1 from DOE95a)

Category	Materials	Waste Material Density (Kg/m^3)		
		Maximum	**Average**	**Minimum**
Inorganics	Iron Based	2.1E+03	8.3E+01	0.0E+00
	Aluminum Based	1.0E+03	1.2E+01	0.0E+00
	Other Metals	1.4E+03	2.7E+01	0.0E+00
	Other Inorganic	2.1E+03	3.9E+01	0.0E+00
Organics	Cellulose	9.6E+02	1.7E+02	0.0E+00
	Rubber	6.8E+02	2.1E_01	0.0E+00
	Plastics	8.9E+02	5.3E+01	0.0E+00
Solidified Materials	Inorganic	2.2E+03	1.3E+02	0.0E+00
	Organic	1.4E+03	8.4E+00	0.0E+00
Soils		1.6E+03	5.7E+00	0.0E+00
Container Materials	Steel		1.4E+02	
	Plastic/Liners		3.3E+01	

Using the average values from this table, the waste material density in a drum is 550 kg/m^3. Based on the statutory waste volume, the total weight of waste in the repository would be about 97 million kilograms (210 million pounds). The waste containers will add another 170 kg/m^3 to the inventory or 30 million kilograms (66 million pounds).

4.3.4 Identification of Significant Radionuclides

In addition to information on physical and chemical parameters, the WTWBIR also includes information on the radioactivity associated with the wastes. The estimated radionuclide inventories in the WTWBIR, scaled to statutory capacity, are:

- CH-TRU — 3.60 million curies
- RH-TRU — 2.11 million curies

Details are included in Table 4-6.

Table 4-6. Major Nuclides in Disposal Radionuclide Inventory
(Source: WTWBIR, Revision 1, Table 4-2)

NUCLIDE	TOTAL CH-TRU (Ci)	TOTAL RH-TRU (Ci)
Am-241	2.23E+05	5.30E+02
Ba-137m	5.03E+03	3.10E+05
Cs-137	5.32E+03	3.28E+05
Pu-238	1.89E+06	3.53E+03
Pu-239	3.85E+05	6.41E+03
Pu-240	7.22E+04	1.74E+02
Pu-241	1.01E+06	9.06E+02
Sr-90	4.07E+03	6.68E+05
U-233	1.38E+03	8.57E+02
Y-90	4.07E+03	6.68E+05
TOTAL, major nuclides	3.60E+06	1.99E+06
TOTAL, all nuclides	3.60E+06	2.11E+06

Virtually all (i.e., 99.4%) of the CH-TRU radioactivity is associated with only five nuclides—Am-241, Pu-238, Pu-239, Pu-240, and Pu-241. In the case of RH-TRU, 93.5% of the curie inventory is attributable to four fission products (Cs-137, Sr-90, Y-90, and Ba-137m) with half-lives of 30 years or less. Because most of the RH-TRU inventory is composed of nuclides with short half-lives, DOE has estimated that the contribution of RH-TRU to the total radionuclide inventory in the repository will decline from about 37% initially to about 1% after slightly more than 200 years (DOE95b). Based on the specific activity of the five major CH-TRU nuclides, the total quantity of these radioactive materials in the WIPP is about 7,000 kg or about 0.005% of the total inventory mass. The total quantity of other very long-lived uranium and thorium radionuclides is about 104,000 kg.

Accurate data on the fractional abundance of each radionuclide contained in TRU waste are necessary because differences in solubility, mobility, and half-life determine the extent to which specific radionuclides reach the accessible environment in a given scenario. The behavior of uranium isotopes U-233 and U-234 provides a good example of the importance of understanding the radionuclide composition of TRU wastes in assessing their potential migration to the accessible environment. In the 1992 performance assessment (SAN92), U-233 and U-234 were estimated to comprise approximately 0.06 percent of the initial inventory, yet they accounted for about 21 percent of the projected discharge to the accessible environment (for the E1E2 scenario at 1,000 years with fracture flow, matrix diffusion, and no retardation). Accurate determination of the uranium inventory is thus very important, even though its quantity is minor compared to plutonium and americium radionuclides.

4.3.5 Determination of Actinide Solubility Limits

Actinide solubility in the Castile or Salado brines that come in contact with the waste is generally thought to be one of the most important parameters for calculating releases to the accessible environment (SAN92). Because actinide solubility is not well understood, there is considerable uncertainty in estimating the quantities of plutonium, americium, and uranium in solution. Estimates of the solubilities of actinide species expected in TRU wastes had a range of 13 orders of magnitude in the 1992 performance assessment (SAN92). The mean, median, and range of values used in SAN92 were obtained by expert elicitation.

In addition to pure solubility (where solid material is dissolved in the liquid) which can be affected by brine salinity, pH, Eh, and the presence of chelating agents and other chemical constituents, there are concerns and greater uncertainty about the possible concentrations of colloidal dispersions (very fine particles in the 0.001 to 0.1 μm diameter range that can remain suspended in the liquid). Colloid formation was not considered in the 1992 PA (SAN92).

To provide more defensible information, DOE has been conducting laboratory experiments on actinide solubility and colloid formation under the Actinide Source Term Program (ASTP) (LOS93, NOV94a, NOV94b). The ASTP has been using small-scale laboratory experiments to develop a conceptual model of actinide solubility. DOE intends to verify this model using large-scale tests (the Source Term Test Program-STTP) with TRU wastes. These tests are currently in process at Los Alamos National Laboratory (LANL). Questions remain regarding the extent to which these studies are representative of actinide mobility in TRU wastes under disposal conditions. For the final Compliance Certification Application, DOE is proposing to include a look-up table which will define solubilities in various environments.
The solubility (or dissolved species) model is an "equilibrium thermodynamic model based on the Pitzer formalism for activity coefficients in concentrated electrolytes" (BYN95). The dissolved species model is developing experimental solubility data, in brines of various compositions and ionic strengths, for five actinide elements—americium, neptunium, thorium, uranium and plutonium in four valence states—+III, +IV, +V, and +VI. Ultimately, the dissolved species model is expected to provide to performance assessment the solubility for these five actinide elements as a function of:

- oxidation state
- brine type
- pH
- pCO_2
- organic ligands

The partitioning of the actinide elements between the four possible oxidation states must also be specified for PA. In recent modeling studies, solubility ranges of 1 to 10^{-10} were assigned for all oxidation states with median values ranging from 10^{-7} moles per liter for +IV to 10^{-4} moles per liter in the +VI oxidation (SNL95). Suggested oxidation state distributions in the same study were:

- Americium — all +III
- Thorium — all +IV
- Uranium — 0 to 20% +VI, balance: randomly distributed among +III, +IV and +V
- Neptunium - randomly distributed between +IV and +V
- Plutonium — 0 to 20% +VI, balance: randomly distributed among +III, +IV, and +V

The specification of the oxidation state distribution for each element poses some difficult technical questions. Since the disposal room environment is expected to become anoxic early in the life of the repository, logic would suggest that the actinide elements will exist in their reduced oxidation states (NOV94a). However, research has shown that alpha radiolysis can convert Am+III to Am+V (NOV94a) and the presence of carbonate stabilizes plutonium in the +VI state (REE94). Consequently, DOE chose to use statistical sampling to characterize the mix of oxidation states for the various actinide elements to be included in PA. The STTP may provide additional experimental insight into these distributions (NOV94a).

Based on experimental work under the ASTP currently in progress, DOE plans to refine the data used in the dissolved species model by the end of the first quarter of 1996 and use these data in the final compliance certification application (BYN95).

4.3.6 Determination of Gas Generation Rates

Volatile organic compounds (VOCs) present in TRU waste can vaporize after waste emplacement in the disposal system and create a potential problem for compliance with RCRA regulations. Gases other than VOCs are also expected to be generated in the waste as a result of corrosion, microbial activity, and radiolysis. These processes are expected to produce gases in much greater quantities than from VOCs present in the waste and represent the principal mechanisms of concern in performance assessment.

In PA, it is necessary to evaluate the combined effect of gas generation on waste storage room closure and brine inflow. The pressure resulting from significant gas generation could retard the rates of both room closure and brine inflow. In the absence of any gas generation there would be no retardation of room closure rates or brine inflow. The determination of the rates for room closure and brine inflow requires complex modeling with computer codes where coupling of physical processes is difficult and use of parameters that have not been measured on actual or, in many cases, even simulated waste.

An analysis of the combined effect of room closure and brine inflow requires an assessment of which occurs first. If complete closure occurs before brine inflow, the enclosed space's very low permeability and porosity could effectively minimize any future brine inflow and mixing with waste. The amount of contaminated brine available for release by drilling would thus be minimal. Conversely, if brine inflow occurs before complete room closure, there could be extensive mixing of disposal system contents with brine, creating a significant amount of contaminated brine available for release in a drilling puncture.

Gas generation is also directly related to actinide solubility, discussed in a previous section. Preliminary work under the ASTP indicates that the presence of carbon dioxide gas (CO_2) directly affects the solubility of plutonium, uranium and other actinides under laboratory conditions (SAN93). The applicability of this information to actual TRU wastes under disposal conditions remains to be demonstrated. As previously mentioned, gas generation can also impact the amount of waste spallation associated with drilling events.

Waste components will affect gas generation rates and processes. The amount of gas generated by corrosion is directly related to the quantity and type of metal present in waste and waste containers, the surface area of the waste, and available moisture. The amount of gas generated by microbial activity is related to the amount of available moisture and cellulosic material (e.g., paper, cloth, and wood). Radiolytic gas generation is a function of the amounts of alpha radioactivity, moisture, and cellulosic material present.

The initial liquid content of the waste may be important to its gas generation characteristics (SAN92). Table 3-1 of the WIPP WAC notes that, as a guideline, residual liquid in well-drained containers should be restricted to approximately one volume percent of the internal container, with the aggregate amount of residual liquid less than one volume percent of the external container (DOE91). The residual liquid limit could be checked in three ways:

- Upon assembly of the drum by personnel at the waste generator site;
- By radiography performed on site by waste generators during the drum certification process
- During visual examination of a container, as applicable

While the combination of these three techniques appears adequate to meet the residual liquid criterion, the use of one technique alone may not suffice. For example, radiography has not been demonstrated to be a fail-safe method for detecting containers of liquids within a waste drum. In January 1993, a full 8-ounce can of adhesive was missed by an operator conducting Real-Time Radiography (RTR) at INEL, and later discovered during the visual examination of the drum contents. Radiography detects movement of liquids within a container; therefore a completely full container could be missed.

4.3.6.1 Average Stoichiometry Model

The average stoichiometry model was used to calculate quantities of gas generated in the 1992 performance assessment (SAN92). DOE also plans to use this model for calculations in the final Compliance Certification Application (NOW95). The average stoichiometry model is part of BRAGFLO—a computer code which calculates two-phase flow in the repository. Thus, brine and gas flows into and out of the repository are coupled to gas generation (i.e., pressure). Sufficient gas pressure can also cause fracturing of the nearby anhydrite layers increasing their permeability. In addition, BRAGFLO uses a porosity surface developed by the SANCHO/SANTOS computer codes to simulate room closure. This porosity surface is a function of the amount of gas present at any point in time. In this way, gas generation is also coupled to the geomechanical behavior of the disposal rooms.

The average stoichiometry model considers the anoxic corrosion of ferrous materials and the anaerobic degradation of cellulosics and rubbers, and calculates the quantity of gas generated and the quantity of water consumed. DOE has discussed the fact that aluminum and its alloys could behave in a similar manner to ferrous materials, but have not included aluminum corrosion in the model.[20] The model does not include possible gas consuming reactions nor does it address other possible gas producing mechanisms such as radiolysis.

[20] Based on the information contained in Table 4-5, it can be estimated, using average values, that the amount of hydrogen produced from ferrous metal corrosion could range from 6.9 to 9.2 x 10^{8} moles depending on which corrosion reaction occurs and assuming the presence of sufficient water to consume all the iron. Similarly, the amount of hydrogen produced by the corrosion of all of the aluminum would be 1.2 x 10^{8} moles or 11 to 14% of the amount from iron corrosion. However, using the maximum values in Table 4-5, the contribution from aluminum would be more than 50% of the total hydrogen. These calculations assume that 1.5 moles of hydrogen are generated for each mole of aluminum consumed.

Two possible anoxic corrosion mechanisms are considered in the model:

$Fe + 2H_2O = Fe(OH)_2 + H_2$ (1)
$3Fe + 4H_2O = Fe_3O_4 + 4H_2$ (2)

Equation 2 produces 33% more hydrogen per mole of iron consumed than does equation 1. Because uncertainty exists as to which equation prevails, DOE has chosen to treat the stoichiometry of the reaction as an uncertain variable which is sampled over the range of possible values for performance assessment calculations. To do this, the two equations above are combined into an "average" equation as follows:

$$Fe + ((4+2x)/3)H_2O = (4-x)H_2 + (3x)Fe(OH)_2 = ((1-x)/3)Fe_3O_4$$

The values of x are assumed to be uniformly distributed between 0 and 1 for Latin Hypercube sampling purposes in PA.

Inundated corrosion rates have been developed from laboratory corrosion studies of mild steels for up to 24 months duration in brine solutions with the pH ranging from an initial value of 6.7 to approximately 8.3 at the end of the tests and a nitrogen overpressure of 10 to 15 atm. The measured hydrogen production rates as a function of time were as follows:

3 months — 0.19 moles H_2 per m^2 steel surface per year
6 months — 0.21 moles H_2 per m^2 steel surface per year
12 months — 0.16 moles H_2 per m^2 steel surface per year
24 months — 0.10 moles H_2 per m^2 steel surface per year

SNL recommended that a value of 0.1 moles/$m^2 \cdot y$ (3×10^{-9} moles/$m^2 \cdot$sec) be used as the best estimate (i.e., median value) (BRU94).

To obtain an estimate of the maximum inundated corrosion rate, it was assumed that the actual pH of the brines in the WIPP repository could vary from 3 to 12. Based on work by earlier investigators cited in BRU94, SNL assumed that the anoxic corrosion rate was essentially constant between pH 4 and 10. Outside this range the following pH dependent changes were anticipated: at pH 3, the rate was expected to be higher by a factor of 50; at pH 11, it would be lower by a factor of 0.05; and at pH 12, it would be lower by a factor of 0.005. In addition, it was assumed that the corrosion rate would increase with pressure and at lithostatic pressure the rate would be four times higher than under the experimental conditions noted above. Consequently, the maximum rate for inundated corrosion was set at 4 x 50 x 0.1 or 20 moles/m^2·y (BRU94). This is equivalent to a maximum value of 6.35 x 10^{-7} moles/m^2·sec.

Corrosion rate data for humid environments (i.e, where the steel is exposed to water vapor) were also developed. Based on the amount of brine present in a disposal room at any given time as calculated by BRAGFLO, the relative amounts of steel subject to inundated corrosion and humid corrosion are calculated. For PA purposes, it is necessary to convert these corrosion rates to a volumetric gas generation rate (i.e., moles H_2 per m^3 of repository volume per second). This requires information on the surface to volume ratio of the contents of an average drum. To perform this conversion, SNL assumes that a drum of CH-TRU waste has an approximate area of 4 m^2 and the contents of the drum contribute an additional 2 m^2 (BRU94). If one assumes that the drum and its contents have the same surface to volume ratio (as was assumed by SNL in the past) and the surface area of the drum is actually 4.5 m^2, then, from the current average inventory data in Table 4-5, it can be estimated that the surface area of the ferrous contents of a drum is 2.7 m^2 and the total surface area of steel per drum is 7.2 m^2 which is 20% higher than the value being used in the 1992 PA (SAN92). For microbial reactions, the following highly generalized equation is used to calculate gas generation (BRU94):

$$CH_2O + \text{unknowns} + \text{microorganisms} = (5/3)\text{gas} + \text{unknowns} \qquad (3)$$

CH_2O, a simplified formula for glucose, is assumed to represent various organic materials (cellulosics, rubbers, and plastics) present in the waste which may be subject to microbial degradation. The actual reactions which could occur and the extent to which water is produced or consumed are subject to a considerable amount of uncertainty. The quantity of gas produced could vary from 0 to 1.67 moles per mole of glucose consumed depending on which of several possible reactions is assumed to occur. Consequently, the stoichiometric coefficient is assumed for PA to vary uniformly over this range rather than remain fixed as shown in equation (3) (SAN92). Plastics and rubbers are expected to be generally more resistant to microbial degradation than cellulosics (papers and rags), but may be subject to some radiation-related degradation reducing their resistance to microbial attack. The extent to which rubbers and plastics enter into the gas generation reactions is uncertain, but should be addressed in PA. Similar to the treatment of anoxic corrosion, assumptions were made that microbial degradation in humid environments proceeded at some fraction of the inundated rate. This fraction was assumed to vary uniformly from 0 to 0.2.

4.3.6.2 The Reaction Path Model

SNL has also developed a more sophisticated model to analyze gas generation, called the reaction path model. This model includes treatment of oxic and anoxic corrosion of steels including passivation and depassivation reactions, microbial degradation, radiolysis of brine, and consumption of carbon dioxide by calcium-bearing species. Unlike the average stoichiometry model, the reaction path model uses thermodynamic calculations to estimate phase stability at any point in time. For example, at certain CO_2 fugacities, iron carbonate may form which prevents anoxic corrosion of the ferrous materials. If the CO_2 fugacity is reduced sufficiently, the passivating layer can decompose allowing corrosion to proceed. While SNL has judged this to be the most comprehensive gas generation model (BRU94), DOE decided that the average stoichiometry model will be used for compliance demonstration. This decision is based on the position that PA has shown a low sensitivity to gas generation and the reaction path model is "unnecessarily costly in time and resources for PA calculations" (NOW95). The model will be retained to support calculations related to actinide chemistry.

4.3.7 Establishing the Waste Envelope

For the Compliance Certification Application, DOE will conduct performance assessments using the available information on waste characteristics and waste components, which must demonstrate that the WIPP complies with §191.13 and §194.34. Many of the waste properties will not be precisely known values which can be used for input to PA as constants. Rather, they will be imprecisely known variables for which a range and probability distribution function will be assigned. The PA process will define an acceptable envelope of waste properties which will ensure compliance with the regulations *on a statistical basis*. This is not to say that some individual complementary distribution functions (CCDFs) produced from particular combinations of uncertain parameters may not exceed the limits in §191.13, but it is required that the mean CCDF comply with §194.34(f) (i.e., there is 95% confidence that the mean of the population of CCDFs meets the disposal standards in §191.13).

Once an acceptable waste envelope has been defined through PA calculations, DOE must have procedures in place to ensure that the actual wastes fall within this envelope. It is conceivable that an actual waste component could lie within the range used to develop the waste envelope, but have a different probability distribution function than was assumed in the PA calculations used for compliance determination. Compliance might not then be demonstrable with actual waste. To preclude this possibility, 40 CFR 194.24 contains procedures for showing compliance at the waste envelope limits. These procedures are discussed in Section 4.6.

4.4 METHODS FOR CHARACTERIZING WIPP WASTE INVENTORY

The DOE/CAO Quality Assurance Program Description (QAPD) (DOE95c) is the quality management document that identifies the quality requirements applicable to WIPP waste characterization. The QAPD establishes the minimum requirements for the development of QA programs for the National TRU Programs Office (NTPO) and the generator sites' QAPjPs. The DOE states that the requirements in the CAO QAPD "are based on the QA requirements and criteria contained in 10 CFR §830.120," and that the QAPD is "consistent with applicable Environmental Protection Agency (EPA) requirements" (DOE94d).

As mentioned previously, the controlling document for TRU waste characterization is the TRU QAPP (DOE94b). This document outlines two approaches, one for retrievably stored wastes and one for newly generated wastes. Both approaches are based in large part on the waste classification system presented in the WTWBIR.[21] DOE asserts in the WTWBIR that the Waste Matrix Codes (WMCs) used to categorize wastes have been established based on "grouping wastes with similar physical and chemical properties."[22] In the TRU QAPP, DOE states their rationale for using WMCs to track TRU wastes:

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[21] The waste classification presented in the WTWBIR was initially developed by DOE and was presented in the DOE Waste Treatability Group Guidance (DOE95) which was prepared to meet the requirements of the Federal Facilities Compliance Act (FFCA) of 1993. This approach was used in DOE's Mixed Waste Inventory Report (MWIR) (DOE93).

[22] It should be noted that wastes may be categorized differently depending on the waste management objective, e.g., for purposes of storage, transportation, or treatment. For example, wastes with the same WMC would be stored together due to their similar physical or chemical nature. For transportation, wastes would be grouped according to different requirements, e.g., the requirements of the TRUPACT-II content codes.

> To ensure consistency throughout the DOE complex regarding TRU waste inventory information, TRU waste characterization information will be correlated to the Waste Matrix Codes established by DOE as acceptable to the WIPP facility.[23]

The TRU QAPP states that there are three broad groups of WMCs:

- solid process residues — 3000 series
- soils — 4000 series
- debris wastes — 5000 series

Existing wastes in these three WMCs will be considered retrievably stored wastes and will be characterized directly. Existing wastes in the other WMCs described in Table 4-4 (WMCs 1000, 2000, 6000 and 9000) will require treatment prior to shipment to the WIPP and will then be considered newly generated wastes. Wastes will be characterized for disposal in accordance with the approach outlined below. The Acceptable Knowledge Guidance Manual (DOE95c) states that

> Four broad matrix parameter categories of waste are used to describe the physical form of the waste and to determine TRU waste characterization requirements: homogeneous solids (summary category S3000), soil/gravel (summary category S4000), debris wastes (summary category S5000), and special wastes (summary category S7000).

The Acceptable Knowledge Guidance Manual further states that Series 7000 (special) wastes will be classified as RCRA hazardous in the same manner as the Series 5000 (debris) wastes (DOE94b). For both waste types, the determination of their RCRA hazardous classification will be made using acceptable knowledge alone, without corroborative empirical sampling and/or analysis. A generalized flow diagram for TRU waste characterization is presented in Figure 4-1. The specific approaches for characterizing newly generated and retrievably stored wastes provide statistically derived means to select waste containers from all three WMCs for verification by visual examination, and waste containers from series 3000 and 4000 WMCs for RCRA characterization.

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[23] Many wastes will have other identification codes that are no longer used as well as EPA derived hazardous waste codes assigned to them. This creates considerable confusion.

The steps in characterizing newly generated and retrievably stored waste are as follows:

- establish profiles for waste streams
- using process knowledge, assign waste containers to waste streams
- assign a waste matrix code to each waste stream
- test all waste containers using headspace gas analysis, radiography, and radioassay
- select statistically determined number of waste containers for RCRA characterization and/or visual examination, depending on the assigned WMC
- determine if waste is hazardous and develop a WMC description

In addition, for newly generated wastes, it is necessary to verify that the waste generating processes have operated within the profile's established administrative controls.

The information listed above must be coordinated with a consideration of the manner in which the waste stream is defined. The definition applicable to TRU waste is found in DOE's Acceptable Knowledge Guidance Manual (DOE95c), and is of fundamental importance to TRU waste characterization because "waste characterization and DQO activities are performed on a waste stream basis" (DOE95c). For the purposes of characterization, TRU waste streams are distinguished on the basis of three factors:

- the summary category of the waste (WMC, WMCG, etc.)
- the waste's status (newly generated or retrievably stored)
- the waste gensis (continuous process or batch)

The combination of these three factors determines the waste stream's anticipated variability and the extent of verification required. Additionally, waste streams are identified on the basis of their waste characterization objectives as defined by the applicable regulatory requirements, e.g., RCRA, TRUPACT-II, etc.

DOE's TRU Waste Characterization Program currently consists of the following six activities: radiography, radioassay, headspace sampling and analysis, solid process residues and soils sampling and analysis, visual examination, and use of acceptable knowledge/process knowledge. Other aspects of TRU waste characterization typically involve scientific research (actinide solubility, etc.) to define *waste characteristics* (see Section 4.3.1). Radiography,

Figure 4-1. Generalized Sequence for TRU Waste Characterization radioassay, headspace sampling and analysis, solid process residues and soils sampling and analysis, visual examination are summarized in the sections below, and the use of acceptable knowledge/process knowledge is discussed in greater detail in Section 4.6.

All TRU waste generators currently perform some waste characterization activities on site, although their capabilities vary considerably. The major TRU generator facilities are: Idaho National Engineering Laboratory, Oak Ridge National Laboratory, the Rocky Flats Environmental Technology Site, Savannah River Site, Hanford, Los Alamos National Laboratory, the Nevada Test Site, Lawrence Livermore National Laboratory, Argonne National Laboratory-East, Argonne National Laboratory-West and the Mound Plant (DOE94d). Some of these sites have multiple facilities involved with some aspect(s) of TRU waste generation, characterization, and storage. As indicated in Table 4-7, these sites have a mix of equipment required to perform the analytical techniques listed above.

Table 4-7. Waste Characterization Capabilities of Ten Main TRU Waste Generators

TRU Generator Site	Current Waste Characterization Capabilities
Oak Ridge National Laboratory (ORNL)	RT RA VE SA HG[2]
Hanford (HANF)	RT RA VE[3] HG[3] SS[3]
Idaho National Engineering Laboratory (INEL)[1]	RT RA HG VE SA SS
Argonne National Laboratory-East (ANL-E)	RA HG
Savannah River Site (SRS)	RT RA
Rocky Flats Environmental Technology Site (RFETS)	HG RT RA VE SS SA
Los Alamos National Laboratory (LANL)	RT RA HG VE SS SA
Lawrence Livermore National Laboratory (LLNL)	RA VE HG RA
Nevada Test Site (NTS)[4]	--
Mound Plant (MOUND)[5]	--

RT = Radiography
RA = Radioassay
VE = Visual Examination
HG = Headspace Gas Sampling and Analysis
SA = Solid Residue Analysis
SS = Solid Residue Sampling

[1] Includes Argonne National Laboratory-West (ANL-W).
[2] Expected to have this capability by FY 1996.
[3] Expected to have this capability by 2002.
[4] NTS currently plans to use the mobile TRU characterization system being developed by LANL.
[5] Mound's plans for TRU characterization are currently uncertain.

In general, facilities that either have historically produced or currently manage plutonium or plutonium-bearing wastes as part of their routine operations have radioassay facilities for the purpose of nuclear accountability. These facilities can be used for waste characterization purposes. Los Alamos National Laboratory is currently developing a mobile TRU characterization system for use by small-quantity TRU sites (MAR95). While DOE will require all TRU waste generator sites to be fully capable of certifying their own wastes prior to shipment to WIPP, the specific details and logistics regarding characterization are unavailable at this time.

4.4.1 Radioassay

Radioassay involves a variety of measurement techniques used to determine the radionuclide content of a waste container. Typically, TRU waste generators are most interested in certain radionuclides, specifically actinide or transuranic species. However, for purposes of radionuclide inventory, many other radionuclides are quantified predominantly by measurement of their gamma emission. Generally, TRU waste generators use non-destructive techniques based on neutron or gamma measurements to quantify the
Physical measurements, i.e., inductively coupled plasma/mass spectrometry (ICPMS), are also used, but less frequently. Passive Active Neutron (PAN) counting and Segmented Gamma Scan (SGS) counting are two examples of systems in common use.[24] PAN is used to identify and quantify the odd- and even-numbered isotopes of plutonium by measuring their neutron emission both spontaneously in the passive mode and in response to bombardment within the detector, the active mode. SGS measures the photon emissions from a waste container using a standard intrinsic germanium type of photon detection system coupled with a transmission source, typically Se-75 for assays of weapons grade Pu-239. A container is divided into a number of segments and each segment is assayed with the transmission source to develop a waste drum specific photon attenuation correction factor by segment. Next the drum is measured without the source and the radionuclides of interest are quantified. Computer enhancement of the data provides a more complete assay of the drum's photon emitting radionuclides (Pu-239, Am-241, etc.).

[24] There are other radiometric techniques used for radioassay, such as Pulse Neutron Coincidence Counting (PNCC) and gamma determinations using a simple unsegmented intrinsic germanium type photon detection system. Still other methods are currently under development.

Due to the wide variety of assay systems employed by TRU generators, concerns have been expressed regarding the comparability of radioassay data among DOE sites. partially in response to this, DOE recently implemented a performance demonstration program (PDP) for radioassay techniques comparable in principle to the PDP for Headspace Gas Analysis, described in Section 4.4.3. PDP participants receive a "standard" waste drum with a known activity concentration and isotopic distribution. Each participant analyzes the drum and reports the results to the program coordinator for scoring and statistical evaluation. Participants are required to use the same techniques for PDP samples as they use for actual characterization of TRU wastes and are "qualified" for that specific technique or combination thereof. Qualification is mandatory and must be maintained to enable a site to certify and ship TRU waste to WIPP.

4.4.2 Radiography

Radiography is a nondestructive, non-intrusive qualitative technique used to identify the contents of a waste container. Most DOE sites currently employ Real-Time Radiography (RTR), which uses x-rays and a video system to allow an operator to view the container's contents in real-time. RTR's primary use is to examine and verify the physical form of the waste and to ascertain that a container complies with the specifications of a content code or other physical requirements. The Quality Assurance Objectives (QAOs) for radiography do not address precision or include specific Minimum Detectable Levels (MDLs) because this technique is primarily a qualitative determination (DOE94b). A statistically determined subset of the waste containers examined with radiography will be verified independently by visual examination (DOE94b). The overall approach to visual examination of waste is presented in Figure 4-2.

While radiography is generally effective, certain materials, particularly lead liners, are not readily penetrated by x-rays and render radiography ineffective when they are present in a waste container. DOE has acknowledged this and states in their Waste Characterization Methods Manual (DOE95d) that

> Containers with high density waste (e.g., leaded rubber, cemented sludges) can only be examined at their edges. In addition to this limitation, waste containers that are configured with a lead liner cannot be examined with radiography.

Figure 4-2. Programmatic Approach to Visual Characterization of TRU Waste

As discussed in Section 4.3.6, small containers completely full of liquid intermingled with other waste in a drum can appear to be empty due to the lack of visible fluid movement upon agitation, and may be missed by operators. Radiography has historically been performed manually, which is tedious and labor intensive. However, DOE has been investigating the feasibility of digitizing the current analog information obtained with RTR and hopes to realize sufficient gains in efficiency to allow installation of an automated system at INEL and possibly at other sites. DOE has made the point that there is "no equivalent or associated method found in EPA sampling and analysis guidance documents." There are other industries that use radiography and may have protocols applicable to DOE. DOE further states in their Waste Characterization Methods Manual that:

> Standardized training requirements for radiography operators are based on existing industry standard training requirements and comply with the training and qualification requirements of ASME NQA-1, Element 2, except for Supplement 2S-2 (DOE95d).

There is no DOE-wide formal certification or accreditation process for radiography operators and each site specifies how it will achieve the training requirements and QAOs presented in the TRU QAPP in their QAPjP.

4.4.3 Headspace[25] Sampling and Analysis

Headspace sampling and analysis are the determination of the chemical composition and concentration of flammable gases, volatile organic compounds, and other gases contained in the void volumes of waste containers. These compounds are determined by gas chromatography and/or gas chromatography-mass spectrometry. TRU wastes are typically packaged in 208 liter (55 gallon) drums. The drums contain 90 mil polyethylene liners, and inside each liner is a 208 liter polyethylene bag that may contain many other smaller bags. Sampling within a waste container can occur in three general areas: in the innermost layer of confinement, i.e., any of the small bags within the drum's interior; in the spaces within the drum liner; and under the drum lid, in the space between the drum lid and the sealed drum liner. The 3-year-old WIPP Performance Demonstration Program for Headspace Gas

[25] The term "headspace gas" should be interpreted to mean hydrogen, methane, and the volatile organic compounds that exist within a layer of confinement in a TRU waste container (DOE94b).

Analysis is detailed in DOE92. This program is used to qualify DOE TRU generators to certify TRU waste containers for shipment to WIPP. Once a participant is qualified using a technique(s), the participant may characterize waste containers for shipment to WIPP using only that same analytical technique(s) used to analyze the PDP samples. participation is mandatory and blind samples are distributed to all participants annually.

4.4.4 Solid Process Residues and Soils Sampling and Analysis

Solid process residue and soil sampling and analysis are used to determine the hazardous constituents in TRU wastes classified as solid process residues and soils (Series 3000 and 4000 WMCs). Sampling procedures are based on methods found in EPA's SW-846 (EPA86) and are detailed in the Methods Manual (DOE95d). The analytical procedures to be used are also based on SW-846, but were modified by Los Alamos National Laboratory for this purpose. A facility for these analyses is presently operational at Oak Ridge National Laboratory. The DOE intends to use sampling and analysis primarily to verify characterizations made using process knowledge.

4.4.5 Visual Examination

Visual examination is the characterization of the contents of a waste container by physical removal, inspection, and sorting for the purpose of establishing or verifying that the correct waste codes have been assigned. In this time-consuming, hands-on process, the contents of a drum are unpacked, examined, segregated if necessary, and repackaged. Several TRU generators have modified facilities that can be used for this purpose. However, it is not clear whether DOE will require each TRU waste generator to have this capability on site or if certain sites would be designated to perform this function for others. Argonne National Laboratory-West has a waste characterization chamber designed for visual examination of waste containers. DOE considers visual examination to be a means of verifying assumptions made using process knowledge, e.g., correct waste code assignment and absence of non-conforming items (residual liquids, compressed gases, etc.). For newly generated wastes, DOE intends to use process knowledge and prospective documentation of each waste container's contents to ensure each container's compliance. For all TRU wastes (newly generated and retrievably stored), DOE says that

> As a QC check, a statistically significant portion of the certified waste

containers must be opened and visually examined. (DOE94b)

The actual number of containers examined must be empirically derived by each site annually, and DOE asserts that

> The number of waste containers requiring visual examination will ensure that the Program is 80-percent confident that, if the indicated number of waste containers is examined, the UCL_{90} of the miscertification percentage will be less than 14 percent, (i.e., there is only a 10-percent chance that the miscertification rate is greater than 14 percent). (DOE94b)

4.4.6 Use of Acceptable Knowledge/Process Knowledge[26]

Each of the above techniques is intended to complement the waste characterization data generated using process knowledge. DOE intends to rely heavily on process knowledge for most WMCs and to use it as the primary means of waste characterization for newly generated waste and retrievably stored WMC 5000 wastes (DOE94b). DOE anticipates that retrievably stored waste will require more frequent verification by empirical techniques to certify wastes in accordance with all applicable requirements. Because process knowledge is such an important element in waste characterization it is discussed in detail in Section 4.5 below.

4.5 USE OF PROCESS KNOWLEDGE (ACCEPTABLE KNOWLEDGE) TO CHARACTERIZE TRU WASTES

4.5.1 Definition and Regulatory Precedent For the Use of Process Knowledge (Acceptable Knowledge)

The DOE recently released guidance to address the use of acceptable knowledge/process knowledge for the characterization of TRU wastes (DOE95c). This guidance document provides the following:

- definitions for acceptable knowledge and process knowledge

[26] The term *process knowledge* has historically been used to refer to what DOE currently calls *acceptable knowledge*. As defined by DOE (DOE95e) and discussed in the text, acceptable knowledge is a broad category of types of information that includes process knowledge.

- guidance to distinguish types of waste streams for waste characterization purposes

- classes of acceptable knowledge

- Quality Assurance requirements for the use of acceptable knowledge to characterize TRU wastes

- specific requirements for acceptable knowledge documentation

The document summarizes DOE's approach to the use of process knowledge for characterizing TRU wastes that previously was scattered among many DOE and CAO documents (DOE94b, DOE94e, DOE95c). In this document, DOE has followed EPA's approach of defining *process knowledge* as a subset of acceptable knowledge (EPA92). DOE defines acceptable knowledge as follows:

> *Acceptable knowledge* includes process knowledge and results from previous testing, sampling, and analysis associated with the waste. Acceptable knowledge includes information regarding the raw materials used in a process or operation, process description, products produced, and associated wastes. Acceptable knowledge documentation may include the site history and mission, site-specific processes or operations, administrative building controls, and all previous and current activities that generate a specific waste.

DOE also states that-

> Acceptable knowledge refers to information that can be used for waste characterization in lieu of waste sampling and analysis conducted in accordance with the requirements specified in the Transuranic Waste Characterization Quality Assurance Program Plan, and may include process knowledge and the results of previous surrogate waste sampling and analysis.

DOE defines process knowledge as follows:

> *Process knowledge* is a term used by the EPA to refer to detailed information on a waste that is obtained from existing published or documented waste analysis data or studies conducted on hazardous wastes generated by process[s] similar to that which generated the waste. Process knowledge describes the process or operation that generated the waste that is being characterized. Process knowledge is used to identify specific constituents in a waste stream and the method (or process) by which the constituents are used that created the final waste.

The precedent for the use of waste-related information in waste characterization originates in the Resource Conservation and Recovery Act (RCRA). Under RCRA, a waste generator is allowed to use "acceptable knowledge" to determine whether a waste is hazardous (EPA94). As stated above, process knowledge is one form of "acceptable knowledge." DOE has determined that "when used in conjunction with other waste characterization techniques" acceptable knowledge "is appropriate to obtain the required TRU waste characterization information" (DOE95c). This information encompasses many aspects of TRU waste, including WMC, physical form, and assignment of a waste container to a specific waste stream. This information will be required to determine compliance with the acceptance criteria from the WIPP WAC, TRUPACT-II, and the TRU QAPP.

Historical definitions of process knowledge within the EPA-regulated community of RCRA waste generators typically include two important aspects:

- they were used solely for the purpose of determining that a waste is hazardous under RCRA; and
- they focused on engineering assessments of waste streams where waste characterizations were based on computational methodologies that were documented, such as mass balance or process engineering diagrams.

While DOE's definition includes these aspects and others, it is not clear that DOE's use of process knowledge is completely consistent with RCRA. In the TRU QAPP (DOE94b) and the Transuranic Waste Characterization Acceptable Knowledge Guidance Manual (DOE95c), DOE outlines the main purposes for the use of process knowledge, including:

- sorting newly generated and retrievably stored waste containers into waste streams;
- estimating the volume and weight of a waste container's contents;
- determining if WMC Series 3000 & 4000 wastes exhibit toxicity characteristics as specified in 40 CFR part 261, Subpart C, in conjunction with empirical sampling and analysis;
- determining if WMC 5000 Series wastes are RCRA hazardous in the absence of empirical sampling and analysis;
- selecting the appropriate method to quantify a waste drum's radionuclide content; and

- describing waste stream continuous processes and changes over time.

4.5.2 Using Process Knowledge for Waste Characterization

The credibility of using process knowledge ultimately rests upon the user's ability to provide the appropriate support documentation. This documentation must demonstrate that the waste producing process was adequately controlled during waste generation to allow the use of information as opposed to empirical investigation. The DOE has proposed eight classes of acceptable knowledge (DOE95c). These are summarized in Table 4-8.

For newly generated and retrievably stored wastes, DOE plans to assign waste containers to a waste stream based on process knowledge after first developing a profile for each waste stream (DOE94b). DOE describes this approach in the TRU QAPP. Waste stream profiling assumes that the waste-generating process is a well-defined and controlled process that can be supported by sufficient documentation, and that the documentation is available and amenable to direct inspection.

Table 4-8. Classes and Examples of Acceptable Knowledge

Class of Acceptable Knowledge	Examples of Supporting Information

waste generating process information	process flow diagrams, documented inputs/outputs, process controls, operating procedures
engineering and design information	piping and glove box designs, equipment and holding tank specifications
supporting data	surrogate waste sampling and analysis data, comparable waste stream analytical data
supplemental data	data obtained from research and development operations, effluent monitoring data, product quality control data
expert knowledge	personnel interviews, site inspections, test or research plans
standard industry practice information	vendor information, material safety data sheets, common industrial operations or treatment practices
compliance program information	RCRA permits, safety analysis reports, chemical inventory databases
program management information	Quality Assurance Plans, procurement documents, operating procedures, waste certification procedures

Important aspects of waste stream profiling include consideration of the following:

- whether multiple profiles are required for complex waste streams

- profile's responsiveness to changes in the waste producing process(es)

- quantification of the uncertainty associated with each part of the profile

- how each stream's profile would be determined, i.e., using average concentration values of specific constituents, or by establishing a range of acceptable concentrations

- reconciliation of a waste stream's profile with an out-of-specification analysis of a specific drum originating in the stream

- protocol required when a waste stream was found to be outside of the profile

It should be noted that much of the waste for which DOE uses acceptable knowledge/process knowledge as the main waste characterization tool originates from non-routine types of activities that are not typically understood to be controlled processes, with well-defined feed materials, intermediate products and outputs. Example are wastes from unscheduled maintenance and the cleanup of chemical or radioactive spills. Acceptable knowledge/ process knowledge may be a poor choice as a waste characterization tool for these and other similar types of waste.

4.5.3 Use of Acceptable Knowledge/Process Knowledge for TRU Inventory

The use of acceptable knowledge/process knowledge to characterize TRU wastes is advantageous for several reasons:

- to minimize worker radiation exposure;

- the physical nature of many wastes (i.e., WMC Series 5000 and 7000 wastes) does not lend itself to conventional SW 846 type analytical procedures; and

- many historical wastes were generated prior to the establishment of RCRA, and are inadequately characterized according to current standards.

As discussed earlier, DOE currently details its inventory of current and anticipated TRU waste in the WTWBIR. The WTWBIR combines information from the following two documents:

- *Integrated Data Base for 1993: U.S. Spent Fuel and Radioactive Waste Inventories, Projections, and Characteristics*, DOE/RW-0006, Rev. 9, April 1994; and

- *U.S. Department of Energy Distribute of the Phase II Mixed Waste Inventory Report*, May 1994 (MWIR).

The WTWBIR is currently considered the best source for information on DOE's inventory of TRU waste. Process knowledge was used to generate much of the information in this document particularly as the basis for calculating waste volumes and other data. Process knowledge should be used with caution because DOE TRU waste generators exhibit great diversity with respect to waste generation and handling. Additionally, uncertainty estimates associated with process knowledge data and their application are not provided and it is unclear that DOE has sufficiently quantified/evaluated these.

4.5.4 Evaluating the Use of Process Knowledge

The use of process knowledge as a predictive tool for TRU waste characterization has not undergone rigorous regulatory scrutiny. Due to the nature of chemical analyses and the complexity of assigning hazardous waste codes, it is important to assess the appropriateness of comparing waste characterizations made with process knowledge to those made with empirical sampling and analysis.[27] For the purpose of this report, such comparisons have been made and one is discussed below (EPA95).

DOE conducted a 2-year investigation of the correlation between process knowledge and empirical sampling and analysis. This study was completed in 1985 and involved a total of 242 containers of TRU waste, which ranged from new (6 months old) to older waste (12

[27] For example, certain waste streams are classified as hazardous solely by virtue of the presence of a specific chemical(s) within the waste generating process (process knowledge), regardless of concentration. For such *listed wastes*, the inability of a chemical analysis to detect the listed waste does not affect the waste stream's classification as hazardous (EPA94). Waste streams are often assigned waste codes for *characteristics wastes* (D Codes) in a *conservative* manner for the purpose of storage, meaning that if a waste generator thinks there is a reasonable probability the waste could exhibit a specific D Code (process knowledge), it is assigned. However, upon empirical testing, many wastes would not actually test hazardous for all of the D Codes they had been assigned. In both of these examples, the comparison between the waste codes assigned using process knowledge and empirical sampling and analysis is inappropriate.

years old in 1983). Of these, 199 drums and 10 boxes were generated at the Rocky Flats Plant and 33 drums were generated at Los Alamos National Laboratory. All containers were initially shipped to the Idaho National Engineering Laboratory (INEL), where they were assayed nondestructively using RTR. The study's objective was to collect information on gas generation, evaluate various venting devices, examine waste for compliance with the WIPP-WAC and evaluate the adequacy of nondestructive examination as a certification technique. The two-volume document *TRU Sampling Program: Volume I—Waste Sampling and Volume II—Gas Generation Studies* (CLE85) describes the study in detail and provides the investigation's results.

The waste containers had initially been "characterized" at the generator facility (RFP or LANL) by the assignment of a Waste Content Code[28] (see Appendix A to CLE85) prior to shipment to INEL. At INEL, each drum was examined using real-time radiography and radioassay by passive-active neutron counting and the results were recorded. The drums were then shipped to the Rocky Flats Plant, where each drum was completely dismantled within a hot cell for visual examination. The contents were emptied, weighed, and analyzed by radioassay when appropriate, and all results were recorded. This study's main purpose was to determine the adequacy of RTR as a nondestructive characterization technique. However, it also provided an opportunity to evaluate the use of process knowledge as a predictive tool. By comparing the content code assigned by the generator using process knowledge against the "proper" content code assigned after complete hands-on examination of the waste container (the equivalent of sampling and analysis), process knowledge can be evaluated as a tool for assigning the correct content code. Toward this end, the data from this investigation were analyzed statistically and the results are described below.

The Kappa statistic was used to evaluate how well process knowledge was able to classify waste by content code compared to how well the codes would be expected to have been assigned by chance alone (EPA95). In summary, process knowledge assigned content codes much better than would be expected by chance alone, indicating that for these waste containers, process knowledge was effective as a predictive tool for waste classification. It should be noted that DOE's proposed use of process knowledge may not lend itself to this type of verification, in large part because problematic sample matrices do not permit

[28] The Waste Content Codes used for this study were developed prior to TRUCON Codes. TRUCON Codes were intended to include all aspects of waste covered by the Waste Content Codes.

comparisons to be made with sampling and analysis results. DOE has recognized this problem with debris wastes (WMC 5000 series) where process knowledge is the preferred waste characterization technique.

In evaluating the CLE85 study, three caveats should be noted -

1) The waste containers used in the study were not statistically selected and therefore were not necessarily representative of TRU waste, thus limiting the study's applicability.

2) Production and waste handling practices, documentation protocols, assay methods, etc., vary among TRU generators. Because of the lack of established, auditable, uniform criteria for waste characterization by all TRU generators, questions exist regarding this study's applicability. Caution must be exercised in applying conclusions to TRU waste generators or specific waste streams other than those used in this study which originated primarily from Rocky Flats and Los Alamos.

3) This analysis provides information on the ability of process knowledge to assign a content code; no conclusions can be drawn about the ability of process knowledge to provide other important, detailed information (e.g., isotopic distribution, amount of free liquids, gas generation rates). This is particularly true for retrievably stored, older waste, where existing information is sparse.

The study discussed here is the only documented evaluation of the use of process knowledge available at this time. However, additional information exists at INEL, Hanford, Oak Ridge National Laboratory, and the Savannah River Site, where DOE contractors have been attempting to verify waste content codes assigned by process knowledge using other techniques. At INEL alone, DOE has performed radiography and radioassay on approximately 30,000 drums of waste to date, some percentage of which have also been visually examined. The information is not yet available so it is not known what level of documentation exists for these examinations or if other formal comparisons have been made. This information could be very useful to a more comprehensive evaluation of the use of process knowledge as a predictive tool.

4.6 TECHNICAL RATIONALE FOR WASTE CHARACTERIZATION PROVISION OF 40 CFR part 194

4.6.1 General Information on Waste

Section 194.24(a) of the rule requires that DOE provide information on the chemical, radiological, and physical composition of the waste scheduled for disposal at the WIPP including both existing and, to the extent practicable, to-be-generated waste. This description can be based on assays, non-destructive examination, process knowledge and any other appropriate evaluation techniques. This information is needed to anticipate the behavior of the waste in the disposal system.

Description of the radiological composition requires, for each radionuclide present or expected, an estimate of the quantity of radioactivity (curies) at the time of disposal (i.e., when the disposal system is sealed). This could involve setting an upper limit for each nuclide. Demonstration that the waste meets the TRU criterion of 100 nCi/g is also required. In addition, information on the expected drum-to-drum variation in radioactivity levels may be required to model cuttings releases associated with drilling events.

Description of the chemical composition would involve documentation of components which might affect waste containment by affecting waste solubility, colloid formation, gas generation, or gas consumption, inter alia. As has been discussed previously, solubility can be affected by the quantity of organic ligands, the quantity of CO_2-forming constituents, and the quantity of waste constituents which can alter the pH of any intruding brines. To characterize gas generation potential, it is necessary to know the quantities of iron and aluminum alloys, the quantities of combustibles, plastics and rubber, and the quantity of water initially present in the waste.

Description of the physical characteristics of the waste would include information on surface-to-volume ratios of corroding metals, waste density and porosity, waste permeability, weight or volume mix of waste forms such as sludges, metals, paper, rags, etc.

4.6.2 Documentation of Waste Characteristics

§194.24(b)(1) further requires that DOE submit documentation substantiating that all waste characteristics which influence the containment of wastes in the disposal system have been identified and assessed for their impact on disposal system performance. The rule lists, but does not limit the characteristics to such items as solubility, gas generation, ability to form stable colloids, shear strength, and compactability as examples of waste characteristics which must be assessed.

The waste shear strength (shear resistance) used in modeling borehole wall erosion during drilling events was originally deduced by SNL investigators from seabed data, which showed that the shear resistance of such materials was between 1 and 5 Pa, a range quoted to be several orders of magnitude lower than macroscopic soil shear strength (PAR70, BER95). For the 1992 WIPP PA, SNL assigned a range of 0.1 to 10 Pa and a median value of 1 Pa for the shear resistance based on the assumption that the waste would behave similarly to montmorillonite clay (BER95, SAR73). However, this parameter was not sampled over the assigned range in the PA calculations; rather the median value of 1 Pa was used in the CUTTINGS model.

If the flow of the drilling mud between the drill collar and the borehole wall is turbulent rather than laminar, an additional waste characteristic—the surface roughness—is required to calculate the shear stress acting on the waste. In the 1992 PA, the range of expected surface roughness was set at 0.025 to 0.04 m, with a median value of 0.01 m (SAN92). The absolute surface roughness values chosen for PA exceeded those of very rough concrete or riveted steel piping (BER94, STR75).

4.6.3 Documentation of Waste Components

Section 194.24(b)(2) requires DOE to submit documentation substantiating that all waste components which influence the waste characteristics described above in 4.6.2 have been identified, and their impact on disposal system performance assessed. The waste components to be evaluated include, inter alia, metals, cellulosics, chelating agents, water, and total activity (in curies) for each radionuclide present in the waste. Other waste components not specifically listed in the rule which may need evaluation include waste mix (by weight, volume, and/or density), quantities of rubber and plastics, quantities of pH altering constituents, quantities of CO_2-forming and -consuming species, and container-to-container variability in radioactivity level. A summary of waste characteristics likely to be used in performance assessment and the waste components which influence them is presented in Table 4-9. It should be noted that, in many cases, there is no single companion waste component for a waste characteristic. This is because the characteristics are in many cases determined by laboratory experiments which cannot be directly related to on-going measurements of the waste.

Table 4-9. Summary of Waste Characteristics and Waste Components Likely to be Used in WIPP Performance Assessment

Waste Characteristic	Waste Component Influencing Waste Characteristic
ROOM CLOSURE	
Shear modulus	
Bulk unloading modulus	
Yield function constants	
Volumetric strain vs. pressure	Waste mix
Initial waste density	Waste mix
CUTTINGS	
Shear strength	
Absolute surface roughness	
Permeability	
particle diameter	
particle density	
Tensile strength	
BRAGFLO - Flow	
Pore shape distribution parameter(s)	
Residual saturations - liquid and gas	
Threshold displacement pressure	
Intrinsic permeability	
Initial porosity	Waste mix
BRAGFLO - Gas Generation	
Anoxic corrosion rates (humid and inundated)	Quantity of iron (and aluminum)
Microbial degradation rates (humid and inundated)	Quantity of cellulosics
	Quantity of plastics and rubbers
	Quantity of electron acceptors (oxidants) such as SO_4^{2-} and NO_3^{1-}
	Quantities of nutrients (P and N)
Equivalent drum surface area	Surface to volume ratio for iron (and aluminum)
Number of drums per disposal room	
Radiolysis rate	Quantity of alpha emitters
	Initial water content[1]
	Quantity of cellulosics
ACTINIDE MOBILITY	
Solubility - pCO_2	Quantities of CO_2-forming and CO_2-consuming species
Solubility - pH	Quantities of acid and base formers
Solubility - complexing agents	Quantities of complexing agents
Solubility - brine concentration	
Solubility - actinide oxidation states	
Colloid concentration(s)	
SOURCE TERM	
Radioactivity	Quantity of curies for each radionuclide
	Drum-to-drum curie distribution
Actinide concentration	Quantity of each actinide

1 - Influences all gas generation mechanisms.

In addition to identifying and assessing the impact on disposal system performance of all waste components which influence waste characteristics, DOE is required under §194.24(b)(3) to substantiate any decision to exclude consideration of any waste characteristic or waste component because such characteristic or component is not expected to significantly influence the containment of the waste in the disposal system.

4.6.4 Limits on Waste Components

DOE is required to set limits on all significant waste components and show that the WIPP complies with §194.34 and §194.55 based on these limits (§194.24(c)). In doing this, DOE must describe the basis for setting these limits and demonstrate that, when all of these waste component parameters are set at their limit, the mean CCDF obtained will meet the containment requirements of 40 CFR part 191.13 at the 95% confidence limit.

As discussed previously in Sections 4.3.1.1 and 4.3.5, actinide solubility depends on various factors including pH, pCO_2, and presence of organic ligands. If the quantities of pH altering species, CO_2-forming and -consuming species and organic ligands in the waste are determined to be important, DOE is required to set limits on these waste components and demonstrate that the mean CCDF obtained when these components are set at the conservative limits meets the requirements of §194.34. For example, CO_2 tends to stabilize plutonium in the +VI valence state which has high solubility, but CO_2 can be removed from the system by reaction with lime or calcium hydroxide. Thus, the conservative limits would be those quantities of materials which produce the maximum amount of $C0_2$ and result in the least CO_2 removal in this specific example with respect to plutonium.

Once the acceptable limits on the waste components have been set, DOE must establish a system of controls which assures that the waste actually emplaced in the WIPP will fall within these limits. Elements of this system of controls include measurement, sampling, chain of custody, and other documentation. If, as discussed in Section 4.6.1, DOE sets an upper limit on the quantities of each radionuclide, then it will be necessary to show during disposal, that this limit will not be exceeded taking into account uncertainties in the measurements of the curie-content of the waste at the various generator sites.

4.6.5 Quality Assurance

As discussed previously in Section 4.3.7, the components of actual waste may differ significantly from the components that were assumed in developing the waste characteristics for the compliance application. This is especially true, since only about 40% of the total CH-TRU waste has been generated to date. The provisions of §194.24 were developed to ensure that the repository will remain in compliance as long as the waste emplaced is within the established limits. EPA believes that the proposed procedure for bounding the waste characteristics is not overly prescriptive and can be addressed within the sensitivity analysis framework which is an integral part of performance assessment. To enhance confidence in the waste characterization process, all activities and assumptions are subject to the quality assurance requirements of §194.22. Use of process knowledge to quantify waste components is specifically subject to these quality assurance requirements (§194.24(c)). EPA is empowered to use audits and inspections to ensure that the quality assurance requirements are met (§194.24(h)).

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